

ORGANIC CHEMISTRY

TARGET CSIR NET PREVIOUS YEAR SOLUTION'S



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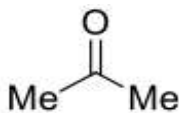
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QUANTA POINT

ORGANIC SPECTROSCOPY

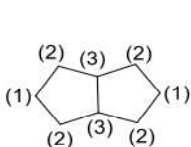
1. **Correct answer : (b)**

Explanation :

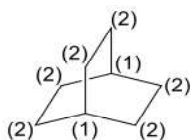


The absorption at 279 nm is due to $n \rightarrow \pi^*$ transition, n stands for non-bonding orbital. The UV region falls in the range of 190-380 nm.

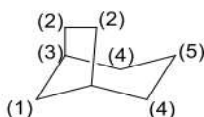
2. **Correct answer : (b)**



3 signals



2 signals

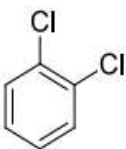


5 signals

The carbons in similar chemical environment give one signal together.

3. **Correct answer: (d)**

Explanation:



Chlorine has two isotopes: ^{35}Cl and ^{37}Cl . They naturally exist in the ratio 3:1.

M: Molecular mass of dichlorobenzene

If both the Cl atoms are ^{35}Cl then ratio will be: $3 \times 3 = 9$

M+2: If Cl at C-1 is ^{35}Cl and Cl at C-2 is ^{37}Cl or vice versa then the ratios add up to be:

$3 + 3 = 6$.

M+4:

If both the Cl atoms are ^{37}Cl then ratio will be: $1 \times 1 = 1$

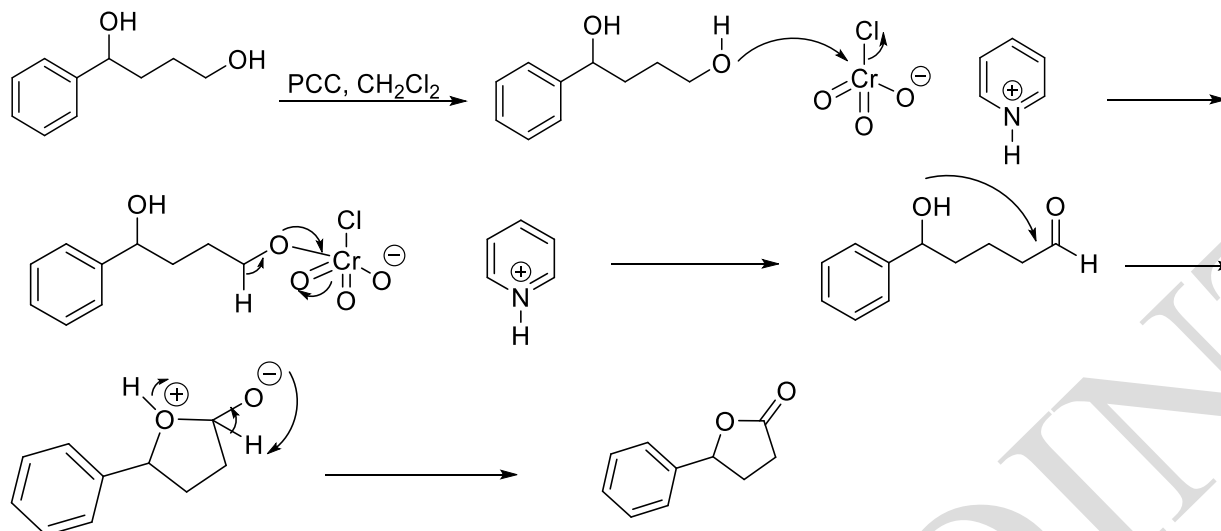
Ratio: 9:6:1

4. **Correct answer : (b)**

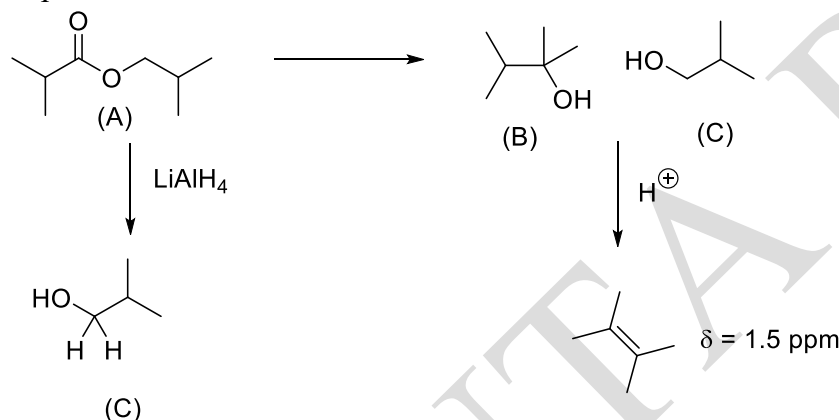
Explanation: The ease of loss of groups increases with size and branching, thus, propyl is lost first, followed by ethyl and methyl.

5. **Correct answer : (d)**

Explanation: PCC stands for pyridinium chlorochromate. It is an oxidizing agent that converts primary alcohol to aldehyde and secondary alcohol to ketone in general. The mechanism of the reaction is shown below:

**6. Correct answer: (a)**

Explanation: The reaction is shown below:

**7. Correct answer: (b)**

Explanation:

For 5 membered cyclic lactones, $\text{C}=\text{O}$ stretching frequency occurs between $1795\text{--}1760 \text{ cm}^{-1}$

$\text{C}=\text{O}$ stretching frequency for:

- Ester: $1750\text{--}1725 \text{ cm}^{-1}$
- Six membered lactone: $1750\text{--}1735 \text{ cm}^{-1}$

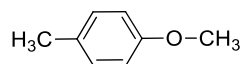
8. Correct answer: (b)

Explanation:

The natural abundance of ^{13}C is 1.1%. In dodecahedron there are 20 carbons. Thus $20 \times 1.1\% = 22\%$. There will be 22% of $M+1$ ($m/z = 261$) signal if M ($m/z = 260$) signal is 100%. The ratio of peaks will be: $100/22 = 5:1$

9. Correct answer: (c)

Explanation:



- Aromatic proton peaks are seen between 6-8 ppm.
- Aliphatic hydrocarbon is seen between 1-2 ppm.
- Aliphatic hydrocarbon attached to electronegative atom occurs downfield and is seen between 3-4 ppm.
- From the data given, the doublet at 6.8 and 7.2 ppm indicates para substituted benzene. The singlet 3H peak at 2.5 ppm indicates methyl group (CH₃) and peak at 3.8 ppm indicates methyl attached to electronegative oxygen (OCH₃).
- The double bond equivalent (DBE) is given by:

$$\text{Degrees of Unsaturation} = \frac{[(\text{Number of Carbons} \times 2) + 2] - \text{Number of Hydrogens}}{2} = \text{DBE}$$

$$[(8 \times 2) + 2] - 10 / 2 = 4.$$

10. Correct answer: (d)

Explanation:

$$\text{DBE: } [(15 \times 2) + 2] - 14 / 2 = 9$$

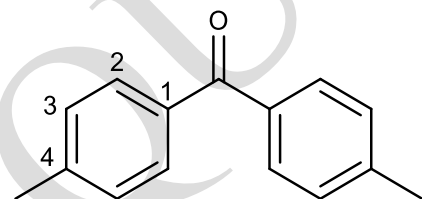
DBE = 9 indicates 2 benzene rings.

The 6 different signals in ¹³C NMR suggest 6 different types of carbon. The signal at 190 ppm is indicative of a carbonyl group.

In the ¹H NMR:

- The peaks at 7.2 ppm and 7.7 ppm are indicative of aromatic protons.
- The two doublets in the aromatic region indicate di-substituted benzene ring at para position.
- The singlet at 2.4 ppm indicates methyl group.

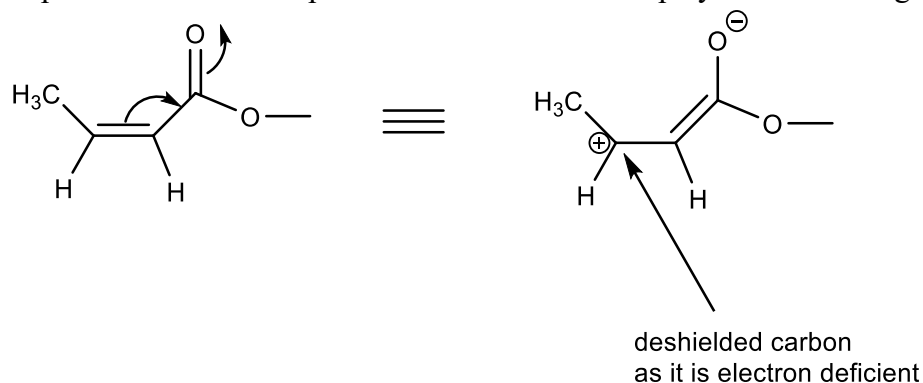
Thus the correct structure is para di-substituted compound.



The carbonyl group and methyl substituent have 1,4 (para) relationship.

11. Correct answer: (d)

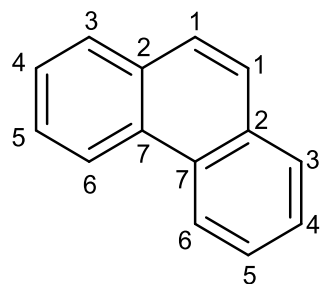
Explanation: The concept of resonance comes into play while deciding the chemical shift of protons.



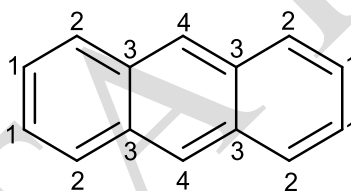
The proton D occurs at 3.9 ppm as it is attached electronegative atom.
The proton B occurs more downfield than proton A due to resonance.
The protons C occurs upfield at 2.1 ppm

12. Correct answer: (c)

Explanation:



Phenanthrene



Anthracene

Carbons with same chemical environment give same signal on NMR. The identical carbons are given the same number in the above structures.

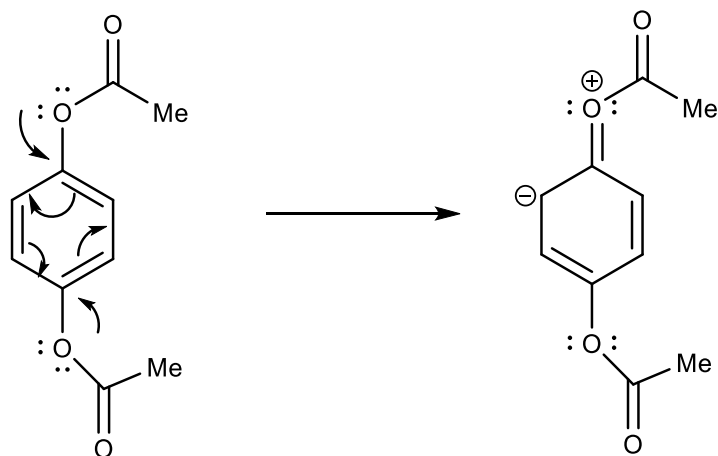
13. Correct answer: (d)

Explanation: The distance between the 2 doublets is: $2.38 - 2.35 \text{ ppm} = 0.03 \text{ ppm}$

$$\begin{aligned} \text{Frequency in Hz} &= \frac{\text{Operating frequency of instrument in MHz} \times \text{ppm}}{10^6} \\ &= \frac{400 \times 10^6 \times 0.03}{10^6} \\ &= 12 \text{ Hz.} \end{aligned}$$

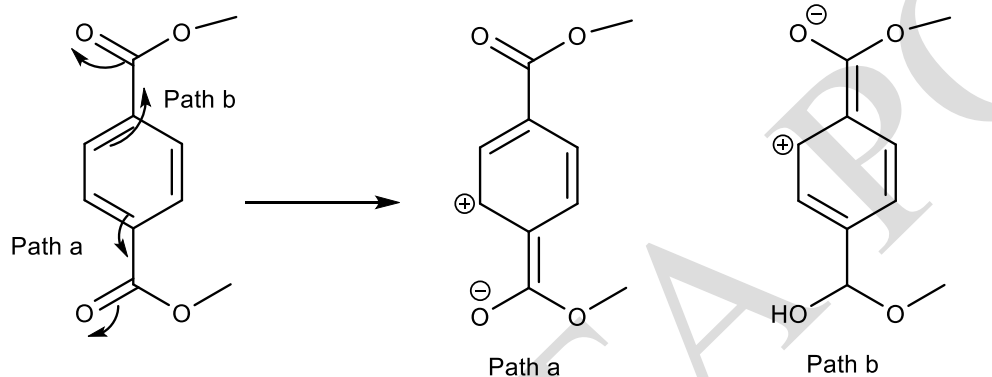
14. Correct answer: (a)

Explanation:



A

The aromatic protons of A are shielded and appear slightly upfield at 6.9 ppm



Ring becomes electron deficient, proton gets deshielded and appears at 7.7 ppm

15. Correct answer: (a)

Explanation:

In ^{13}C NMR:

0-50 ppm: C-C single bond

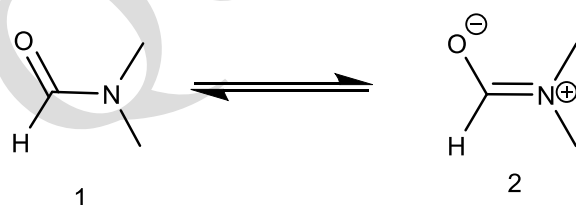
50-100 ppm: C-X (X: O, N, S, and halogen)

100-150 ppm: C=C double bonded carbons

150-200 ppm: C=O (carbon double bonded to electronegative atom)

16. Correct answer: (a)

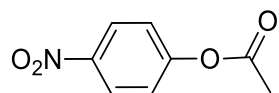
Explanation:



At lower temperatures DMF exists in form (2). The 2 methyl groups are non-equivalent and appear at two different chemical shifts of 2.6 and 2.8 ppm. The olefinic proton appears at a singlet at 7.8 ppm.

17. Correct answer: (d)

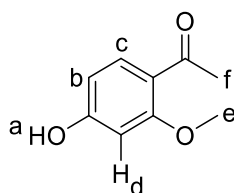
Explanation:



The IR spectra give signal at $1765\text{--}1762\text{ cm}^{-1}$ if oxygen atom is conjugated with alkene or aromatic.

18. Correct answer: (d)

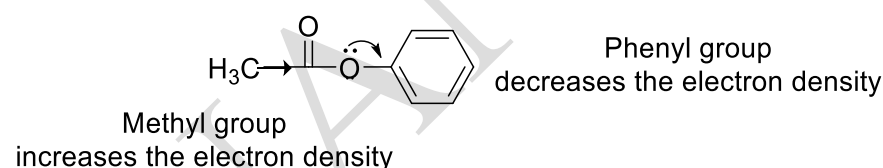
Explanation:



- The methoxy proton (e) appears as a singlet at 3.9 ppm. The methyl proton (f) shows a peak at 2.3 ppm.
- The aromatic protons (b, c and d) appear around 6.5 ppm – 8.0 ppm.
- The OH proton (a) comes around 5.8 ppm.

19. Correct answer: (b)

Explanation:



In IR spectrum, esters show a peak around $1735\text{--}1750\text{ cm}^{-1}$. But due to the presence of phenyl ring the frequency extends up to 1765 cm^{-1} .

20. Correct answer: (c)

Explanation: For Homo annular diene,

Basic value = 253

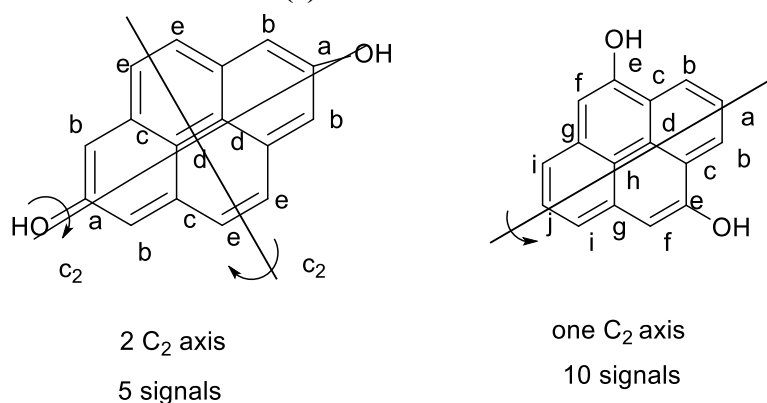
Ring residue = 20

Exo double bond = 5

That adds up to: $253 + 20 + 5 = 278\text{ nm}$.

This value is close to 275 nm. Thus, correct answer is (c).

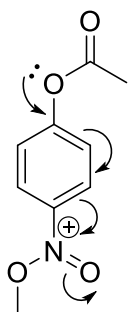
21. Correct answer: (c)



To count the number of signals, pass the C_2 axis and count the number of carbons on either side of the C_2 axis. Carbons on either side of C_2 axis will give same signal.

22. Correct answer: (d)

Explanation:

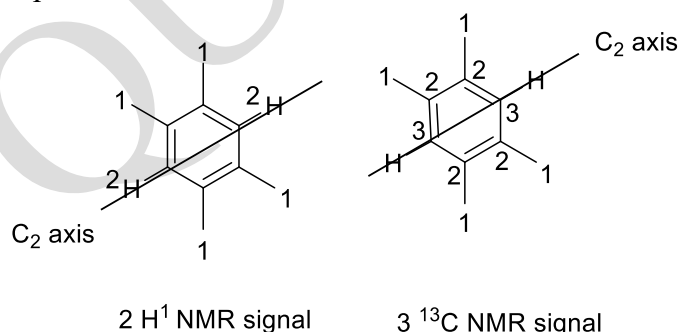


p-nitro phenyl acetate

The carbonyl ester peaks appears at a higher frequency than for a normal ester because of the presence of strong electron withdrawing p-nitrophenoxy group.

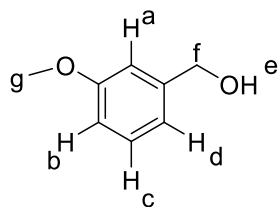
23. Correct answer: (a)

Explanation:



24. Correct answer: (b)

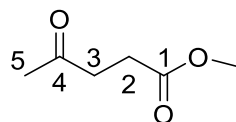
Explanation:



The four distinct aromatic protons (a, b, c, d) give signals ranging 6.9-7.0 ppm. The protons (f) appear at 4.6 ppm as a singlet. The methoxy proton (g) show a singlet peak at 3.9 ppm and the OH proton (e) appears at 5.2 ppm as a singlet.

25. Correct answer: (d)

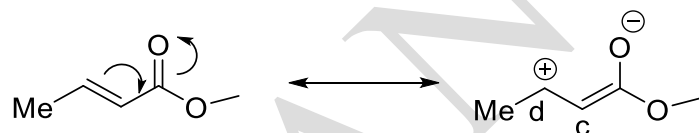
Explanation:



The methoxy group appears at 51 ppm. The aliphatic carbonyl $C=O$ appears above 200 ppm i.e. at 172 ppm whereas ester carbonyl appears below 200 ppm i.e. at 208 ppm. The methyl group carbon appears at 32 ppm.

26. Correct answer: (d)

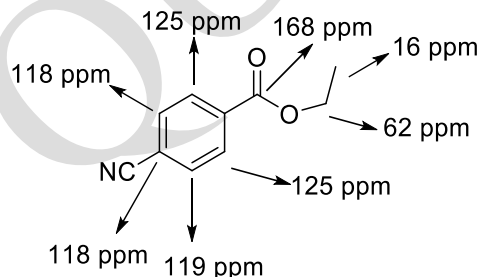
Explanation:



Due to resonance, carbon d appears more upfield than c. Hence (d) is the correct answer.

27. Correct answer: (c)

Explanation:

In ^{13}C NMR:

0-50 ppm: C-C single bond

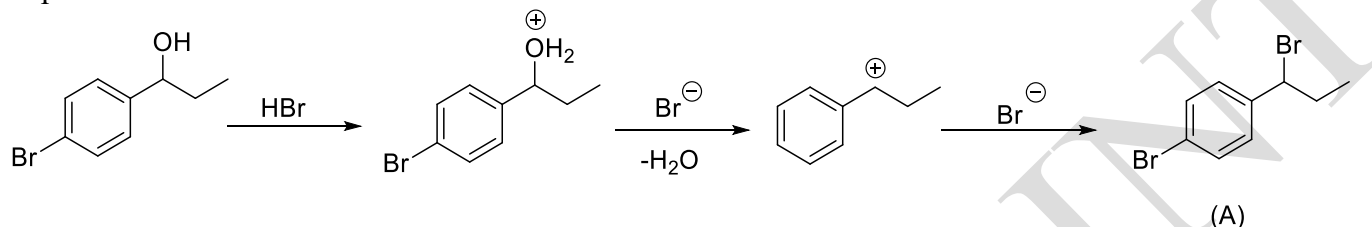
50-100 ppm: C-X (X: O, N, S, and halogen)

100-150 ppm: C=C double bonded carbons

150-200 ppm: C=O (carbon double bonded to electronegative atom)

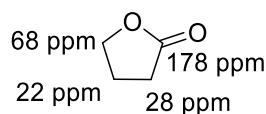
28. Correct answer: (c)

Explanation:



29. Correct answer: (c)

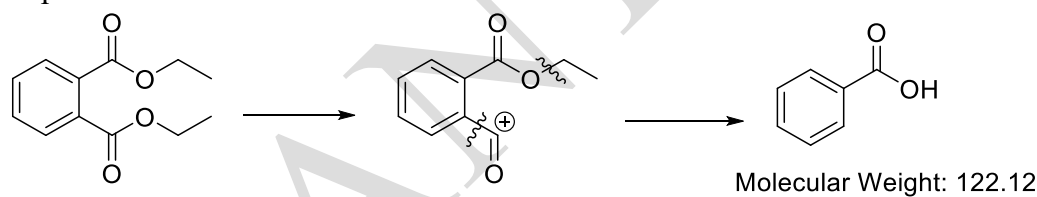
Explanation:



The signals at 28 ppm and 22 ppm indicate that 2 carbons are in similar environment eliminating options (a and d). The carbonyl carbon peak occurs at 178 ppm. There is only one peak at 68 ppm indicating the C-O peak. Thus, the eliminating option is (b).

30. Correct answer: (b)

Explanation:



Mass of metastable ion is given by: $[M_2^2/M_1]$
 $(122 \times 122)/177 = 125.4$

31. Correct answer: (d)

Explanation:

Multiplicity = $2nI + 1$

$n = 3$

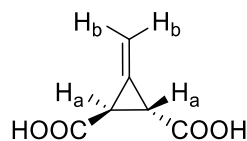
$I = 1$ (for D)

Thus multiplicity = $2 \times 3 \times 1 + 1$
 $= 7$

Thus, relative intensity = 1:3:6:7:6:3:1

32. Correct answer: (c)

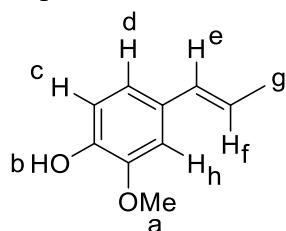
Explanation:



- As there is no signal for methyl protons (3H) in the NMR data, it rules out the possibility of options (a) and (d).
- As mentioned, the product is racemic, thus ruling out the possibility of (b).
- Thus the structure (b) matches with the NMR data. The presence of symmetry in the molecule leads to only two proton signals in ^1H NMR.

33. Correct answer: (a)

Explanation:



- The presence of a broad band at 3400 cm^{-1} confirms the presence of OH group. The OH and NH groups can appear at any ppm in NMR spectra. Here, it appears as a singlet at 5.0 ppm
- The three distinct aromatic protons appearing as a doublet or a singlet only rule out the possibility of option c. The aromatic protons are observed at (c: 6.9 ppm, 1H, d); (d: 6.75 ppm, 1H, d), (h: 6.8 ppm, 1H, s).
- The peak at 3.8 ppm (a) is OMe peak. It appears as a singlet and rules out the possibility of option d.
- $J = 18\text{ Hz}$ indicates trans geometry of H's, thus ruling out option (b). The alkene protons (e and f) appear at 6.28 ppm and 6.0 ppm.
- The methyl protons (g) appear at 1.85 ppm as a doublet.

34. Correct answer: (b)

Explanation:

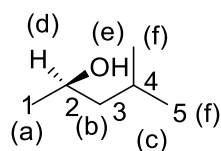
CH_3COCH_3 6H 1 equivalent ($6 \times 1 = 6$) 6H 1	CH_2Cl_2 2H 3 equivalent ($3 \times 2 = 6$) 6H 1 (integration ratio)
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35. Correct answer: (d)

Explanation: The molecules which have a change in dipole moment have intense signals in the IR spectrum.

36. Correct answer: (d)

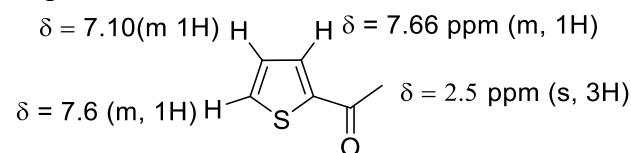
Explanation:



6 signals are observed for NMR of (R)-4-methylpentan-2-ol. The protons of the methyl groups (f) at carbon 4 give the same signal as they have the same chemical environment. The rest of the protons give different signals.

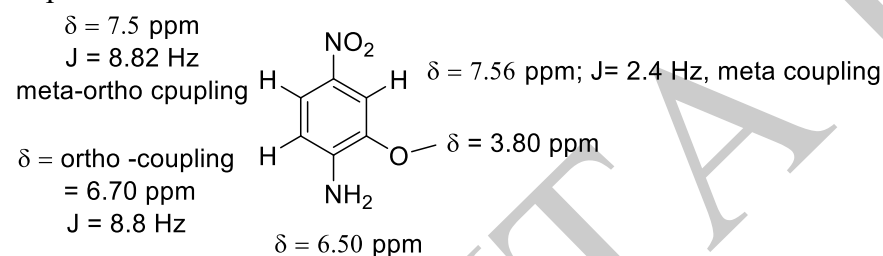
37. Correct answer: (d)

Explanation:



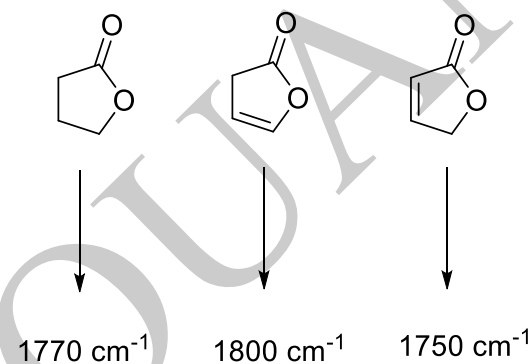
38. Correct answer: (b)

Explanation:



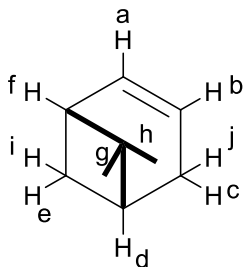
39. Correct answer: (a)

Explanation:



40. Correct answer: (b)

Explanation:



The two methyl groups are diastereotopic.
They are not in the same environment.

41. Correct answer: (b)

Explanation:



Chlorine has two isotopes: ^{35}Cl and ^{37}Cl . They naturally exist in the ratio 3:1.

M: Molecular mass of dichloroethane

If both the Cl atoms are ^{35}Cl then ratio will be: $3 \times 3 = 9$

M+2: If Cl at C-1 is ^{35}Cl and Cl at C-2 is ^{37}Cl or vice versa then the ratios add up to be:

^{35}Cl	^{37}Cl
^{37}Cl	^{35}Cl
3	1
$\times$	$\times$
1	3

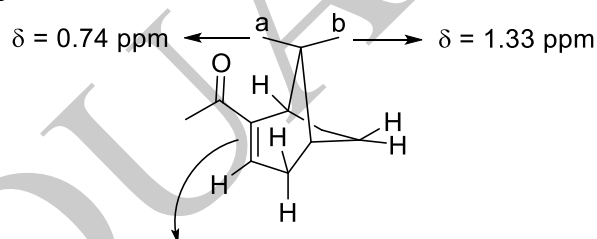
$3+3 = 6$.

M+4: If both the Cl atoms are ^{37}Cl then ratio will be: $1 \times 1 = 1$

Ratio: 9:6:1

42. Correct answer: (b)

Explanation:

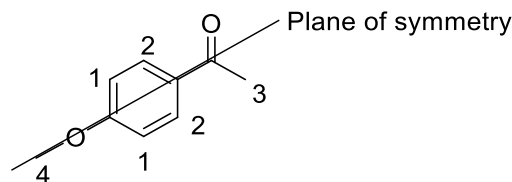


The anisotropic effect of π electrons
differentiates the chemical environment of

Me_a and Me_b . Me_a is slightly shielded as compared to Me_b .

43. Correct answer: (a)

Explanation:



From the spectral data, it can be seen that there is a plane of symmetry in the molecule as the 4 aromatic protons give only two signals.

The -OMe (4) peak appears at 3.8 ppm as a singlet and the Me (3) proton appears as a singlet at 2.5 ppm

44. Correct answer: (a)

Explanation: Frequency in Hz = (Operating frequency of instrument (in Hz) $\times$ chemical shift in ppm)

Chemical shift = Frequency in Hz / Operating frequency of instrument

Average frequency = $(1759 + 1753 + 1747 + 1741) / 4$
 $= 1750$ Hz.

Thus Chemical shift = $1750 / 500 = 3.5$ ppm

Coupling constant J = difference between any two adjacent line frequencies

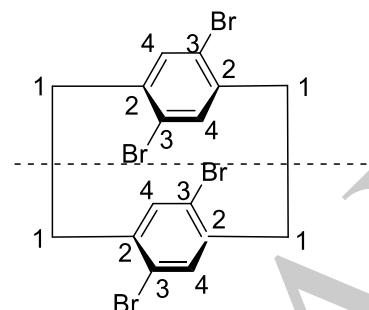
$= 1759 - 1753$ Hz

$= 6$ Hz

45. Correct answer: (a)

Explanation:

The molecule has a plane of symmetry (represented by dotted line). The chemically equivalent carbons give the same signal, thus totally 4 signals are seen for this molecule.



46. Correct answer: (c)

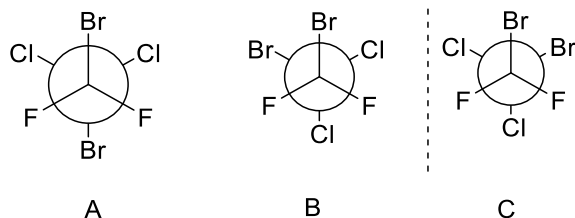
Explanation:

C_6H_6	CH_3CN
6H	3H
1 equivalent	2 equivalent
6H	6H
1	1 (integration ratio)

Molar ratio is 1:2

47. Correct answer: (d)

Explanation:



In conformer A:

Multiplicity: $2nI_F + 1$

$$: 2 \times 1 \times 1/2 + 1$$

$$: 2$$

The conformer B and C are mirror images of each other.

Multiplicity: $2nI_F + 1$

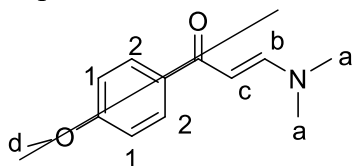
$$: 2 \times 2 \times 1/2 + 1$$

$$: 3$$

Total no of lines: $3 + 2 = 5$

48. Correct answer: (c)

Explanation:



There is plane of symmetry in the molecule. The 4 aromatic protons give 2 signals as doublet.

The protons (a) are chemically equivalent and appear as a singlet at 3.0 ppm.

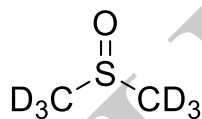
The proton (b) appears as a doublet at 8.0 ppm.

The proton (c) appears at 5.8 ppm as a doublet.

The proton (d) appears at 3.8 ppm as a singlet.

49. Correct answer: (d)

Explanation:



Multiplicity: $2nI + 1$

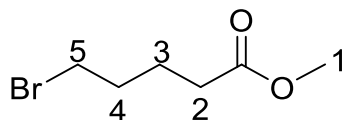
Where n is number of neighboring protons and I is spin number of protons.

For DMSO: $n = 3$, $I = 1$ (for D)

Multiplicity = $2 \times 3 \times 1 + 1 = 7$.

50. Correct answer: (b)

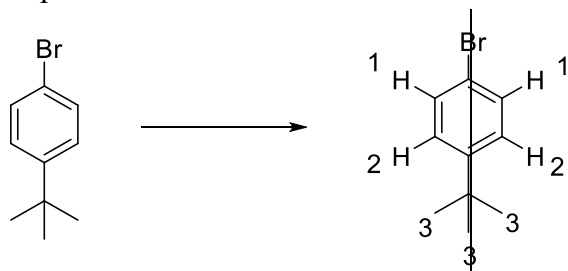
Explanation:



- The OMe protons (1) appear as a singlet at 3.59 ppm.
- The CH₂ protons (3 and 4) appear as multiplets.
- The CH₂ protons (2 and 5) appear as triplets.

51. Correct answer: (a)

Explanation:



Plane of symmetry

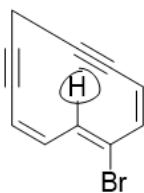
The protons (1) which are closer to Br atom appear at 7.38 ppm.

The protons (2) closer to t-butyl group appear at 7.25 ppm.

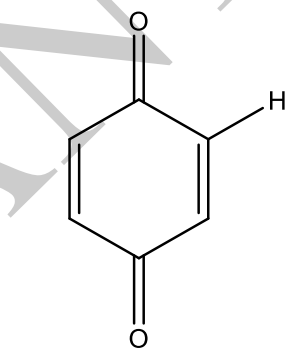
The nine protons (3) of t-butyl group are all equivalent and appear at 1.29 ppm.

52. Correct answer: (b)

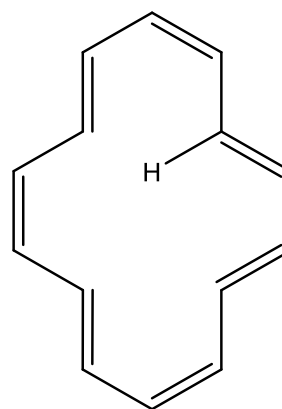
Explanation:



The circled proton will be highly deshielded due to paratropic anisotropy $\delta = 16.4$ ppm. The system is anti-aromatic due to presence of 14 π - electrons.



$\delta = 6.72$ ppm
vinylic proton with EWG



$4n + 2 = 14 \pi e^-$
in delocalization

Aromatic inner proton
will be highly shielded
i.e. diatropic anisotropy
 $\delta = -0.61$

53. Correct answer: (d)

Explanation: A double beam UV-spectrophotometer follows Beer Lambert law but fails for $\text{K}_2\text{Cr}_2\text{O}_7$ when pH is not kept same in all measurements.

54. Correct answer: (b)

Explanation:

Natural abundance

^{32}S 100%

^{33}S 0.79 %

^{34}S 4.4%

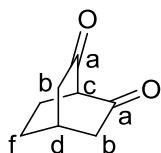
$$M^+ = 100/(100+0.49+4.43) = 0.95$$

$$\% M+1 \text{ peak} = (0.79/0.95) \times 100\% = 0.8 \%$$

$$\% M+2 \text{ peak} = (0.042 / 0.950) \times 100\% = 4.4\% \approx 4\%$$

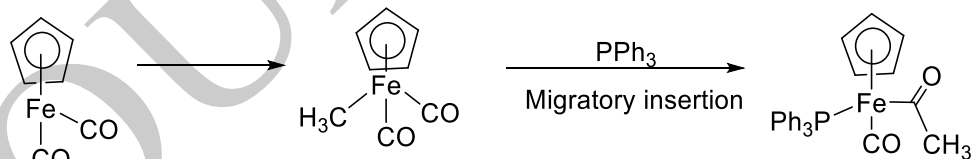
55. Correct answer: (C)

Explanation: There are 6 different types of carbons in this molecule. Thus, 6 signals are observed in its ^{13}C NMR spectrum.

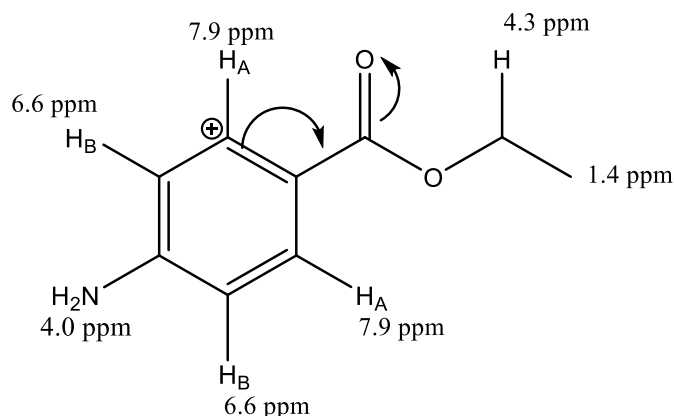
**56. Correct answer: (b)**

Explanation:

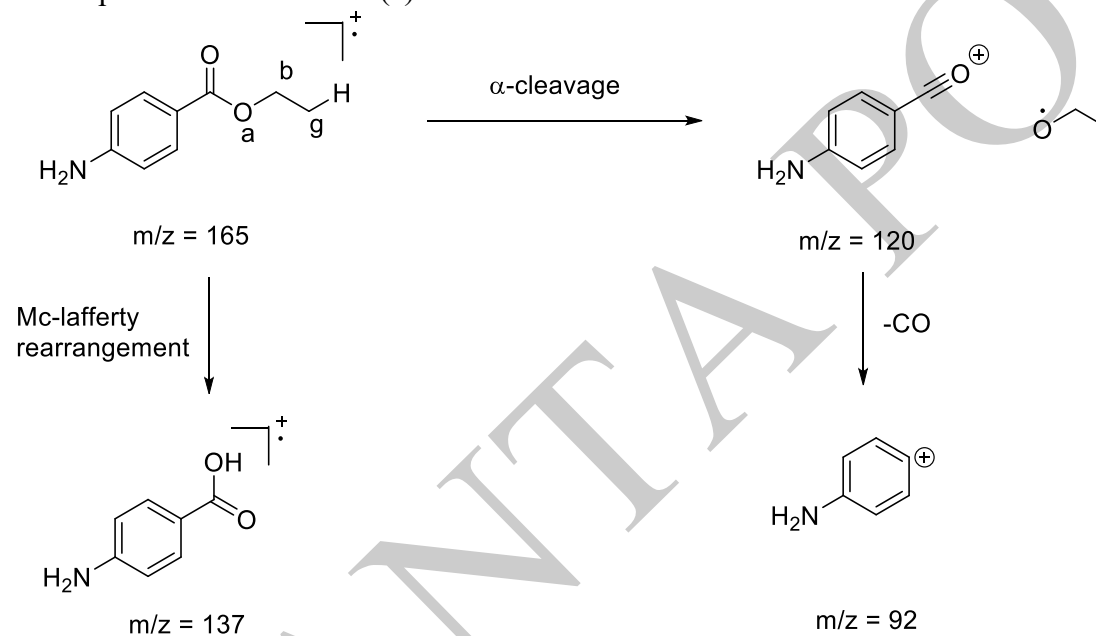
Consider the following reaction:

**57. Correct answer: (a)**

Explanation: From the ^1H NMR spectrum, the chemical shift value $\delta = 7.9$ (d, $J = 8$ Hz, 2H), 6.6 (d, $J = 8$ Hz, 2H) indicates para substituted benzene. Thus, option (c) and (d) are neglected.



Mass spectrum also confirm (a)



58. Correct answer: (a)

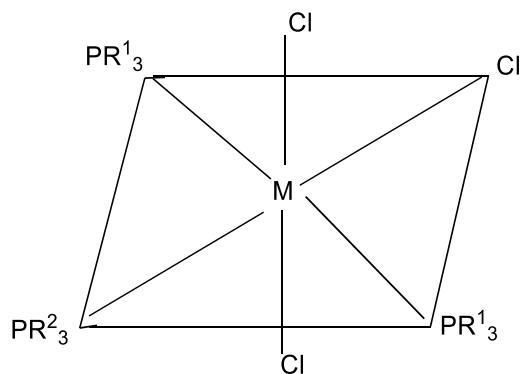
Explanation: For H_A , the chemical shift value will be 5.1.

H_1 and H_7 are more relatively more shielded and thus have lower chemical shift value than the rest.

There is a large chemical shift difference between endo and exo methylene protons, thus H_B is -0.3 ppm.

59. Correct answer: (c)

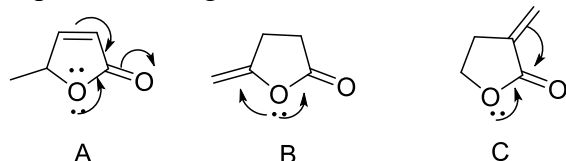
Explanation:



$I = 0$ for M thus metal does not couple with phosphorous during NMR spectra. Since there are 2 types of P atoms present in the complex, 2 peaks are seen in ^{31}P NMR spectrum.

60. Correct answer: (c)

Explanation: Higher the bond order of $\text{C}=\text{O}$, greater the IR stretching.



IR = 1750 cm^{-1}

IR = 1810 cm^{-1}

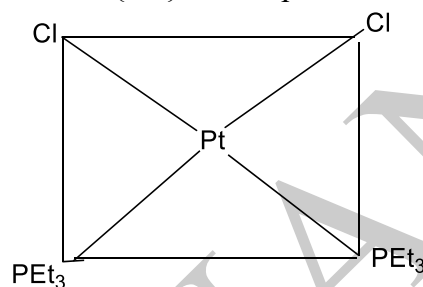
IR = 1761 cm^{-1}

Cross-conjugation in A decreases $\text{C}=\text{O}$ bond order. Thus, IR stretching frequency is lowest for A.

61. Correct answer: (b)

Explanation:

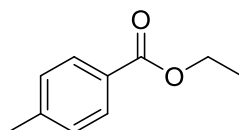
The ^{31}P {1H} NMR spectrum is comprised with satellite peak of a singlet signal.



62. Correct answer: (b)

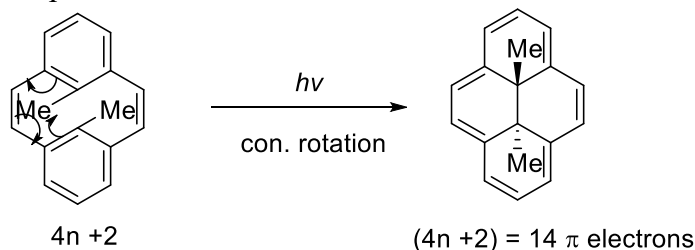
Explanation:

4 signals between 120-150 ppm in ^{13}C NMR spectra indicate p-substitution in aromatic region. 2 doublets between 6.8-8.5 ppm indicate aromatic ^1H . An absorption band at 1724 cm^{-1} indicates the presence of ester functional group in the compound.

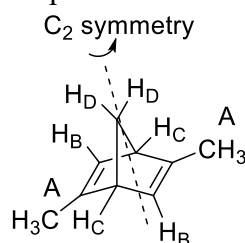


63. Correct answer: (d)

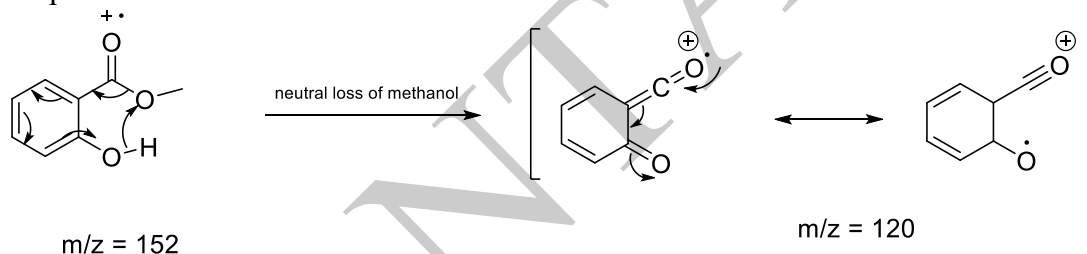
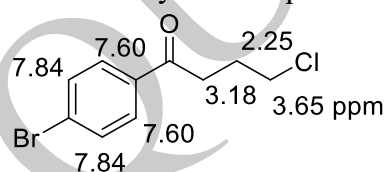
Explanation:

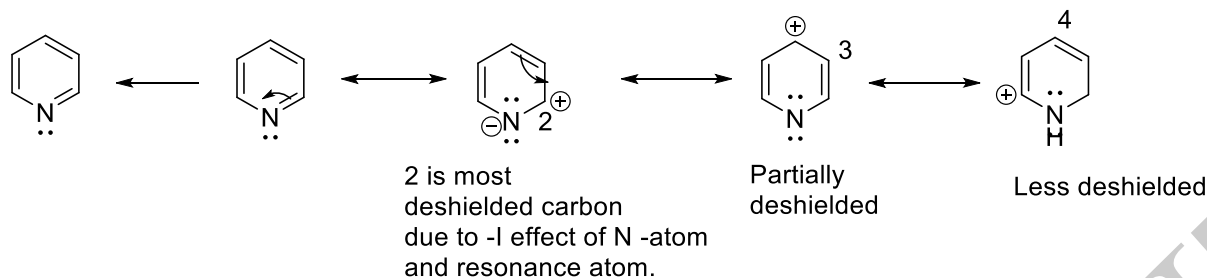


Aromatic, diatropic ring current

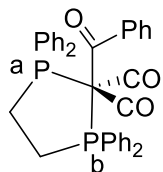
Due to aromaticity, the inner trans methyl groups are seen highly upfield at -5 ppm in ^1H NMR.**64. Correct answer: (b)**Explanation: There are 4 ^1H NMR signals**65. Correct answer: (c)**

Explanation:

Peak at 120 will be due to loss of CH_3OH (mass = 32). Meta and para isomers cannot give CH_3OH loss.**66. Correct answer: (a)**Explanation: The ^1H NMR peaks at 7.84 ppm and 7.60 ppm with integration of 2H and coupling constants 8Hz indicates para substituted benzene. Thus, eliminating option (d).The carbonyl carbon peak at 197 ppm is seen in ^{13}C NMR.**67. Correct answer: (b)**The frequency of absorption of compound having inter-molecular hydrogen bonding decreases, because on dilution the strength of intermolecular H-bonding decreases. Thus OH group absorbs at 3300 cm^{-1} .

68. Correct answer: (c)**69. Correct answer: (d)**

Explanation:



Both phosphorous are chemically different.

Signal for P_a : $(2 \times 1 \times 0.5) + 1 = 2$ (doublet)Signal for P_b : $(2 \times 1 \times 0.5) + 1 = 2$ (doublet)**70. Correct answer: (b)**

Explanation:

$$\nu_{O-H} = 3600 \text{ cm}^{-1}$$

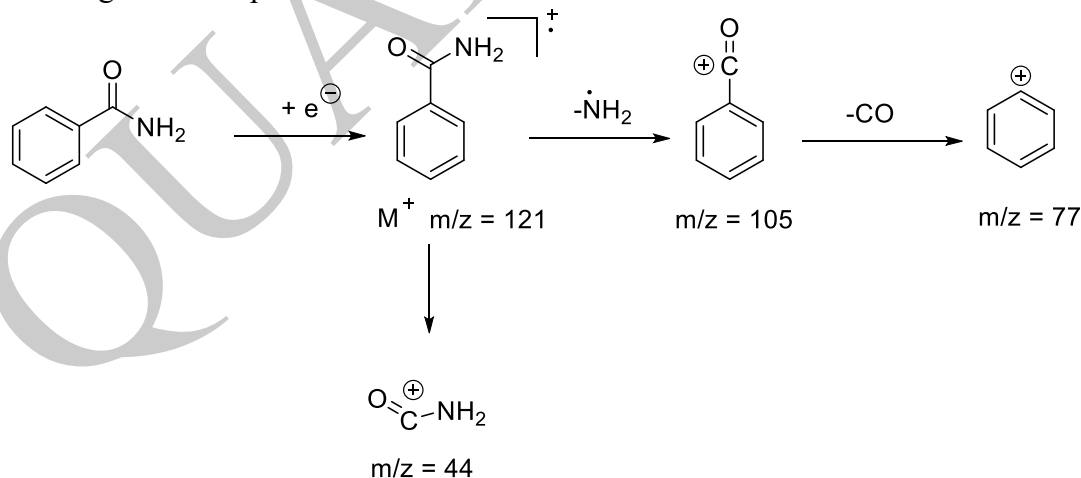
$$\text{Since, } \nu = (1 / (2\pi c)) \times \text{sqrt}(k/\mu)$$

This implies, frequency is inversely proportional to square root of μ .

$$\frac{\nu_{O-H}}{\nu_{O-D}} = \sqrt{\frac{\mu_{O-D}}{\mu_{O-H}}} = \sqrt{\frac{16 \times 2}{16 + 2} \times \frac{(16 + 1)}{(16 \times 1)}} = 2600 \text{ cm}^{-1}$$

71. Correct answer: (b)

The fragmentation pattern is shown below:

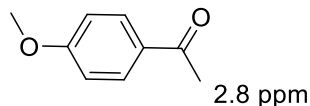


72. Correct answer: (c)

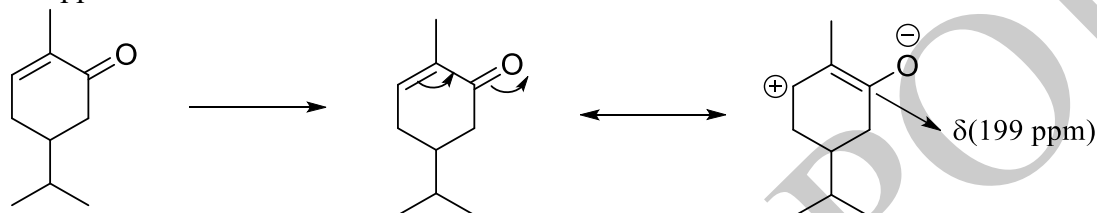
Explanation:

The aromatic peaks at 7.8 ppm indicate para substituted benzene.

3.8 ppm

The ketone carbonyl carbon peak is seen at 197 ppm in ^{13}C NMR spectrum.**73. Correct answer: (d)**

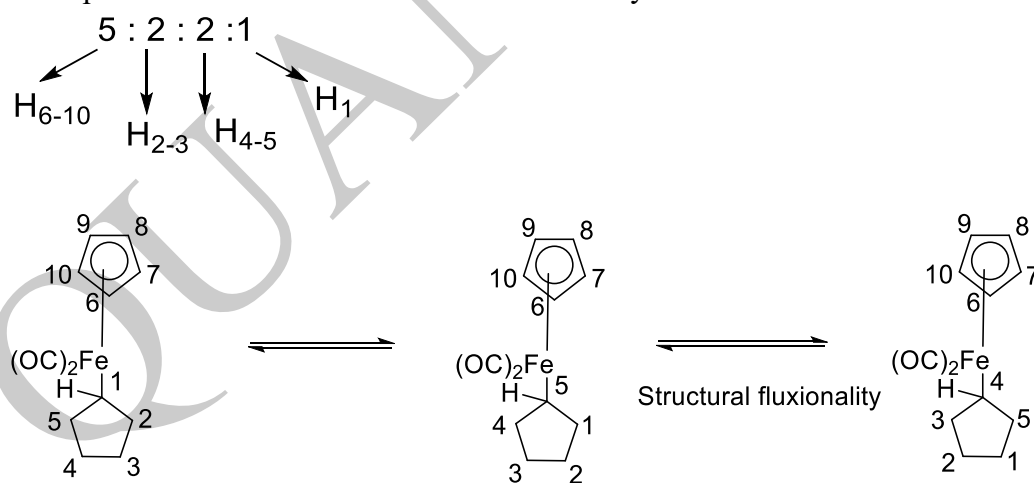
Explanation: The frequency of carbonyl carbon decreases due to resonance and thus the peak occurs at 199 ppm.

**74. Correct answer: (d)**

Explanation: Greater the %s character, greater is the carbonyl stretching frequency. In (B), carbon is sp hybridized having 50% s-character. Hence it has the highest carbonyl stretching frequency $\approx 2140 \text{ cm}^{-1}$. Between A and C, A has more frequency than C because of ring strain in the molecule. Thus, $B > A > C$.

75. Correct answer: (a)

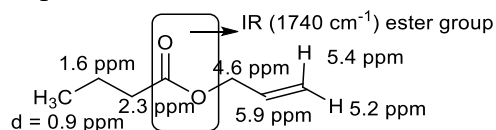
Explanation: At 30°C , the compound shows structural fluxionality. Thus, 2 bonding modes are shown $\sigma(\eta^1)$ and $\pi(\eta^5)$. Hence 2 doublets are seen in ^1H NMR due to $\eta^5\text{Cp}$ and $\eta^5\text{-Cp}$. But 4 peaks are observed at -80°C in the intensity ratio 5:2:2:1.

**76. Correct answer: (d)**

Explanation: Three different IR bands suggest 3 different CO environments in the complex. The terminal carbonyl shows absorption at $2120-1850\text{ cm}^{-1}$ and the ketone carbonyl shows absorption band around $1600-1700\text{ cm}^{-1}$.

77. Correct answer: (a)

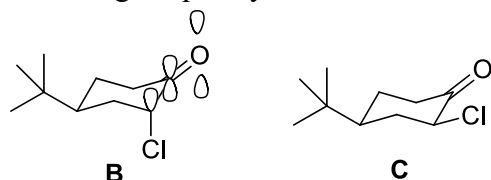
Explanation: The chemical shift values of the protons are indicated in the molecule below.



78. Correct option (c)

Due to presence of ring flipping in A, the stretching frequency will be lowest. In B and C flipping is absent due to presence of bulky group.

In B as the Cl is on axial position hence, orbitals are available for back-bonding and hence C=O frequency will be reduced, whereas in C there is no effect like this, hence C will have highest C=O stretching frequency.



79. Correct option (c)

Chemical shift values of δ (s, 3H), 3.9 (s, 3H) ppm tells that molecule has one CH₃ group and one OMe group. Thus option (a) and (d) are incorrect,

Now, CH₃ group attached to C=O must give peak somewhere around 1.9 ppm, since it is given around 2.4 ppm in the question that tells that CH₃ is attached to benzene ring. Hence correct option is (c)

80. Correct option (c)

As per the given spectroscopic data, the compound has only one type of hydrogen and carbon also the mass is 84. Hence correct option is (c).

81. Correct option (b)

The given molecule $\text{TiCl}_3(\text{CDH}_2)$ will have these NMR active nuclei:

NMR active nuclei	Number of equivalent species (n)	I value
^{13}C	1	$\frac{1}{2}$
^1H	2	$\frac{1}{2}$
D	1	1

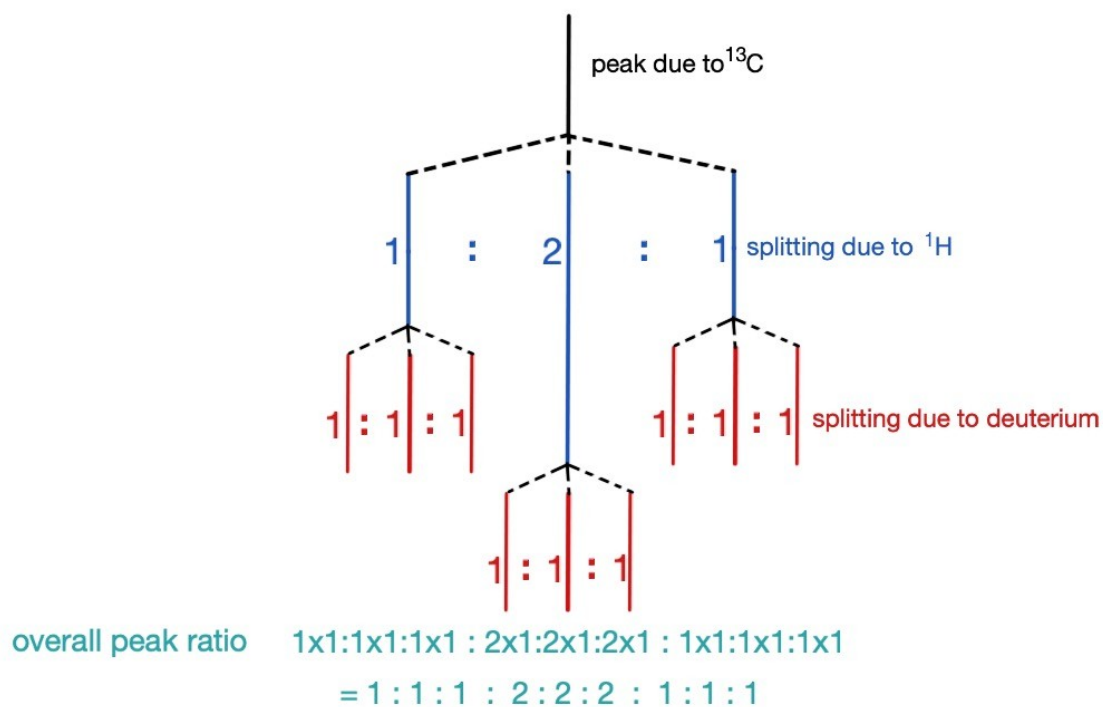
According to given condition $J_{(9::)}^< > J_{(9::)}^<$, ^{13}C NMR will follow splitting pattern in which NMR spectra will be split by Hydrogen and then followed by deuterium.

Number of lines in which ^1H will split peak = $2nI + 1 = 2 \times 1 \times \frac{1}{2} + 1 = 2$

Since it follows Pascal rule, hence peak ratio will be 1:2:1

Number of lines in which Deuterium will split = $2nI + 1 = 2 \times 1 \times 1 + 1 = 3$

Since it does not follow Pascal rule, hence peak ratio will be 1:1:1

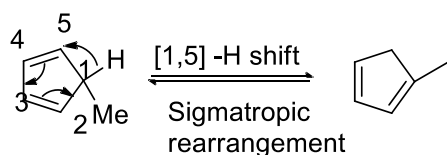


Hence, overall peak ratio will follow pattern shown in option (b)

PERICYCLIC REACTIONS

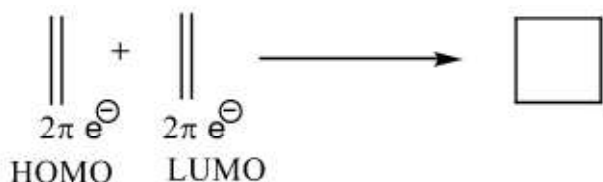
1. Correct answer: (c)

The above reaction is a 1,5 sigmatropic hydrogen shift. That means, the sigma bond migrates from the first atom to the 5th atom. This reaction takes place in presence of heat. The mechanism of the reaction is given below:



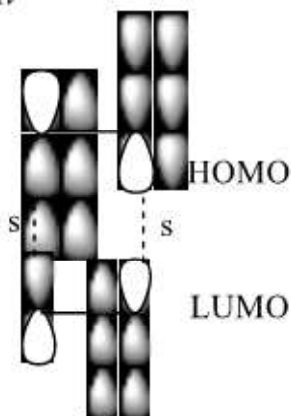
2. Correct answer: (b)

Consider the π molecular orbitals (MO) of the olefins, HOMO (π) – the bonding MO and the LUMO (π^*) anti-bonding molecular orbital (MO). The electronic transition takes place between HOMO of one alkene and LUMO of other alkene under photochemical conditions only. The molecular orbital diagram given below gives a better understanding.



$\uparrow \psi_2$ under photochemical condition,
HOMO and LUMO is ψ_2 orbital.

$\uparrow \psi_1$
 $h\nu$



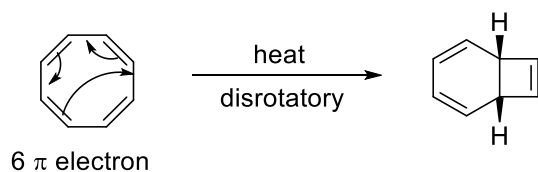
supra-supra interaction takes place.

Thus [2+2] cycloaddition is $\pi_{2s} + \pi_{2s}$ interaction.

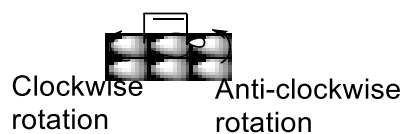
3. Correct answer: (c)

The product X is formed through diels alder reaction and follows the endo rule. The reaction between X and Y is the paterno-buchi reaction.

The endo rule: The diels alder reaction gives bicyclic products when the diene is a ring. If the substituents on the dienophile are 'cis' to each other, the 2 substituents end up going down relative to the carbon bridge in the product, called the endo addition or sticking up towards the carbon bridge called the exo addition. **The Diels alder reaction preferentially forms the endo product as the major product in the formed bicyclic system.**

4. Correct answer: (a)

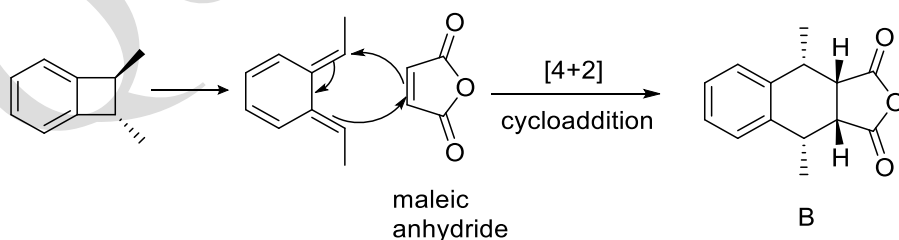
Electrocyclic reaction is a concerted interconversion of a conjugated polyene to a cycloalkene or vice versa. The above reaction should be disrotatory to obtain the given product stereochemistry.



The rotation of atomic orbitals in opposite directions is dis-rotatory motion.

5. Correct answer: (b)

The mechanism of the reaction is given below:

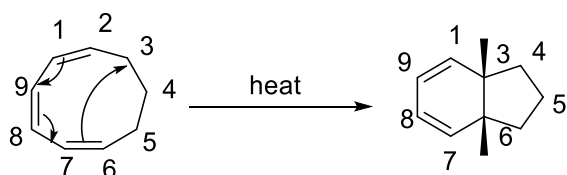


Product B is formed through Diels alder reaction. Diels alder reaction is a concerted, stereoselective and stereospecific reaction that takes place in presence of heat. The diene should be in s-cis configuration for the diels alder reaction. In the above reaction, maleic anhydride (dienophile) reacts with diene to give the diels alder product.

6. Correct answer: (c)

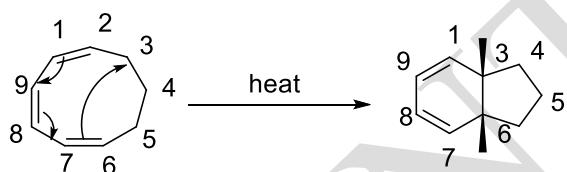
Explanation:

Sigmatropic reaction: It is a rearrangement reaction in which a sigma bond or a group connected by a sigma bond breaks and migrates to the terminus of an adjacent pi electron system. The numbers in the bracket [i,j] refer to the relative position of the atom involved in the migration.



7. Correct answer: (a)

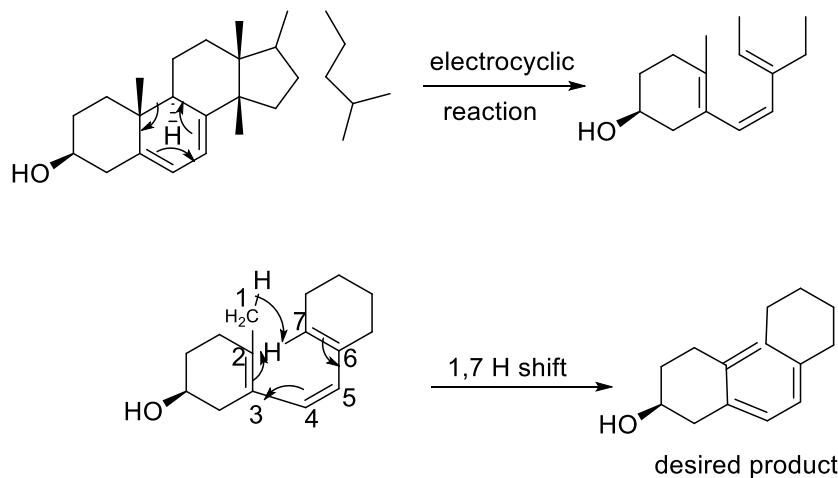
Explanation:



6 π electron participate in a disrotatory process.

8. Correct answer: (b)

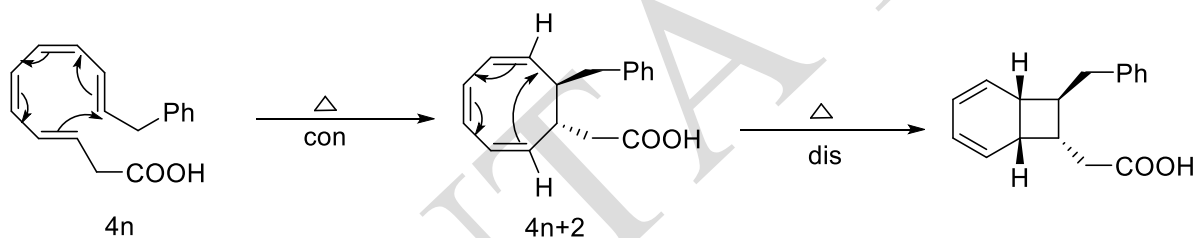
Explanation:



9. Correct answer: (c)

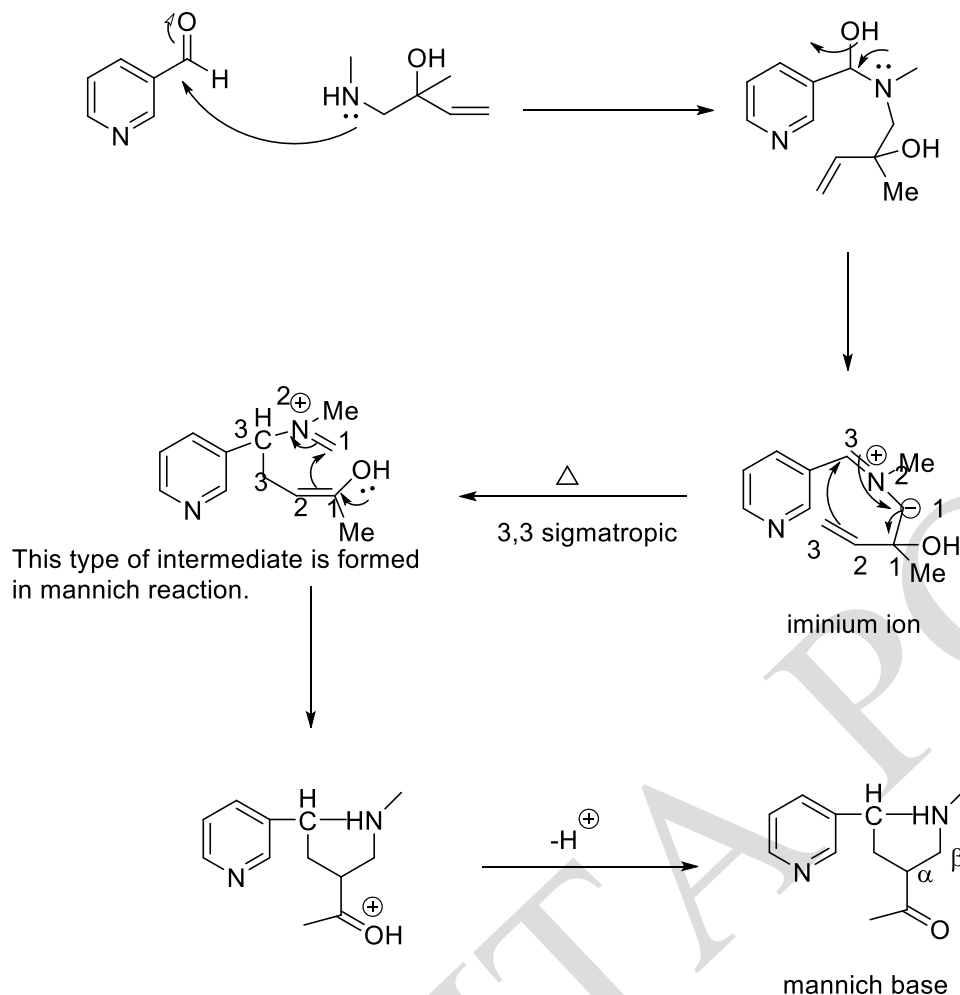
Explanation:

The mechanism of the reaction is illustrated below.



10. Correct answer: (a)

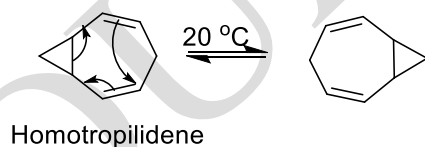
Explanation: The mechanism of the reaction is given below:



The final product in mannich reaction is β -amino carbonyl compound, also known as mannich base.

11. Correct answer: (a)

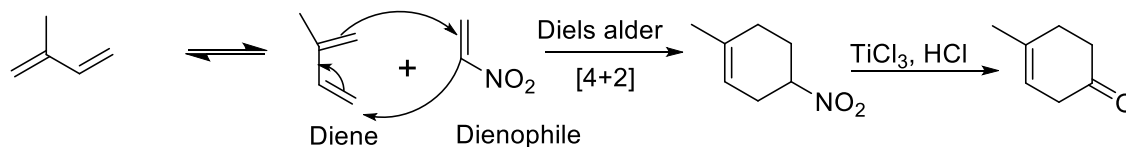
Explanation: The concerted reaction mechanism is shown below.



12. Correct answer: (a)

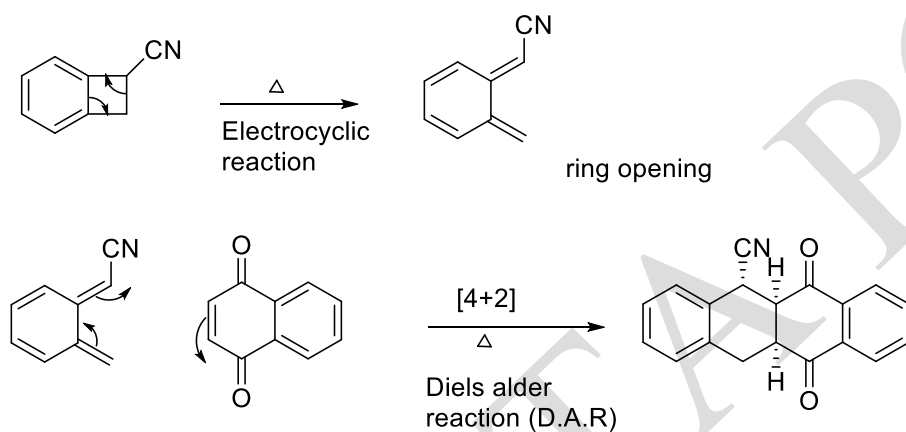
Explanation: In presence of heat, the diene and dienophile undergo a concerted reaction to give the [4+2] cycloaddition (popularly known as diels alder) reaction. The nitro functional group of the formed

product is reduced in presence of TiCl_3 and HCl (McMurry method) to give the final carbonyl compound.



13. Correct answer: (c)

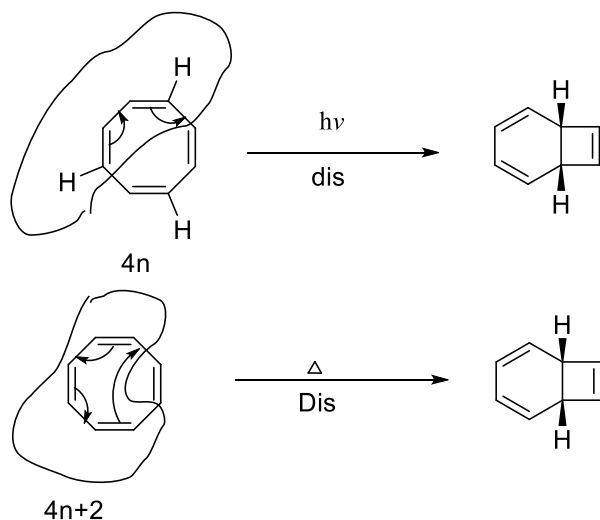
Explanation: The following reaction is a combination of electrocyclic reaction and diels alder reaction. The mechanism of the reaction is given below.



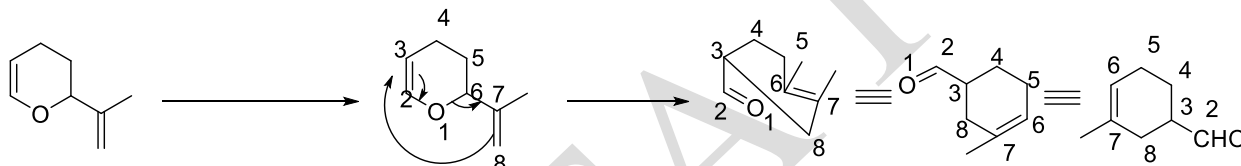
14. Correct answer: (d)

Explanation:

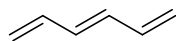
To obtain the appropriate product stereochemistry, dis-rotation takes place in thermal and photochemical conditions.

**15. Correct answer: (c)**

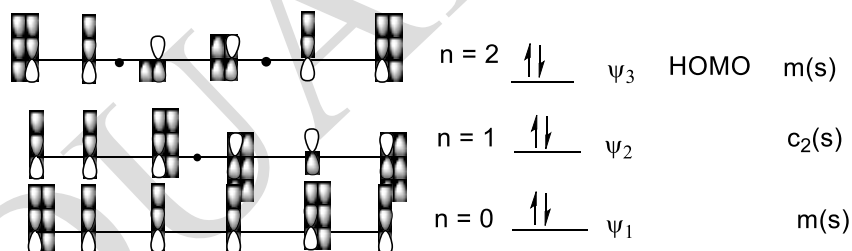
Explanation: This reaction is an example of intramolecular [3,3] sigmatropic rearrangement

**16. Correct answer: (b)**

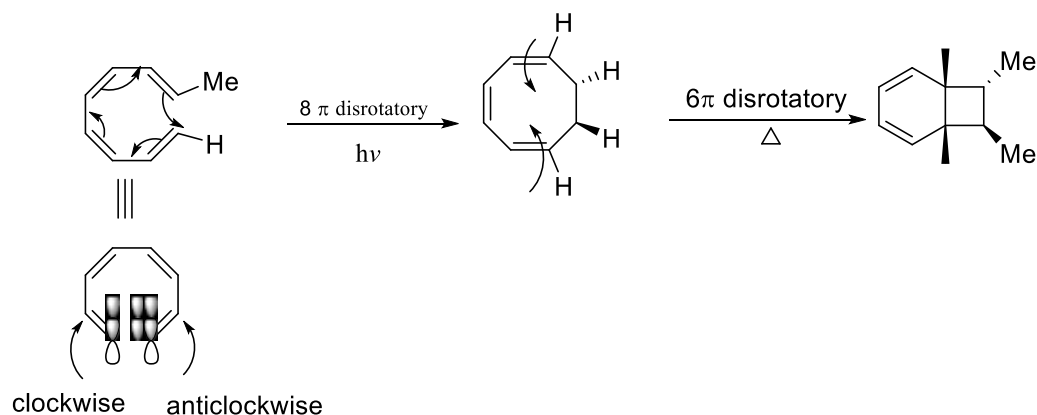
Explanation:



1,3,5 hexatriene

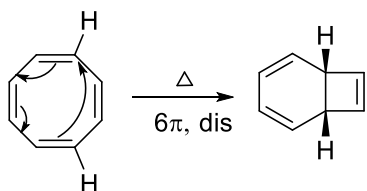
**17. Correct answer: (b)**

Explanation: Ψ_5 is the HOMO of 1,3,5,7 cyclooctatetraene under photochemical conditions. The orbitals rotate in dis-rotatory motion to form the product.



18. Correct answer: (d)

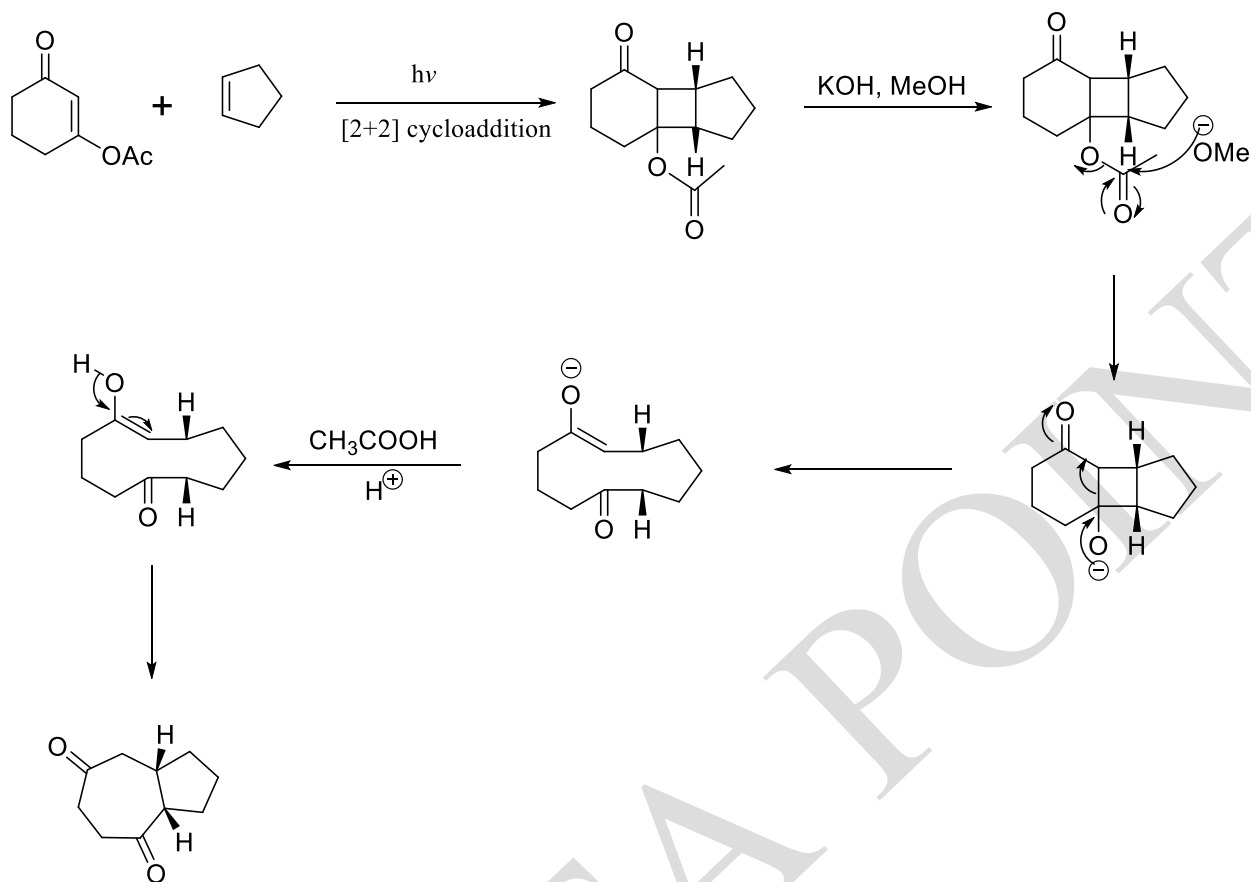
Explanation: The concerted reaction is shown below.



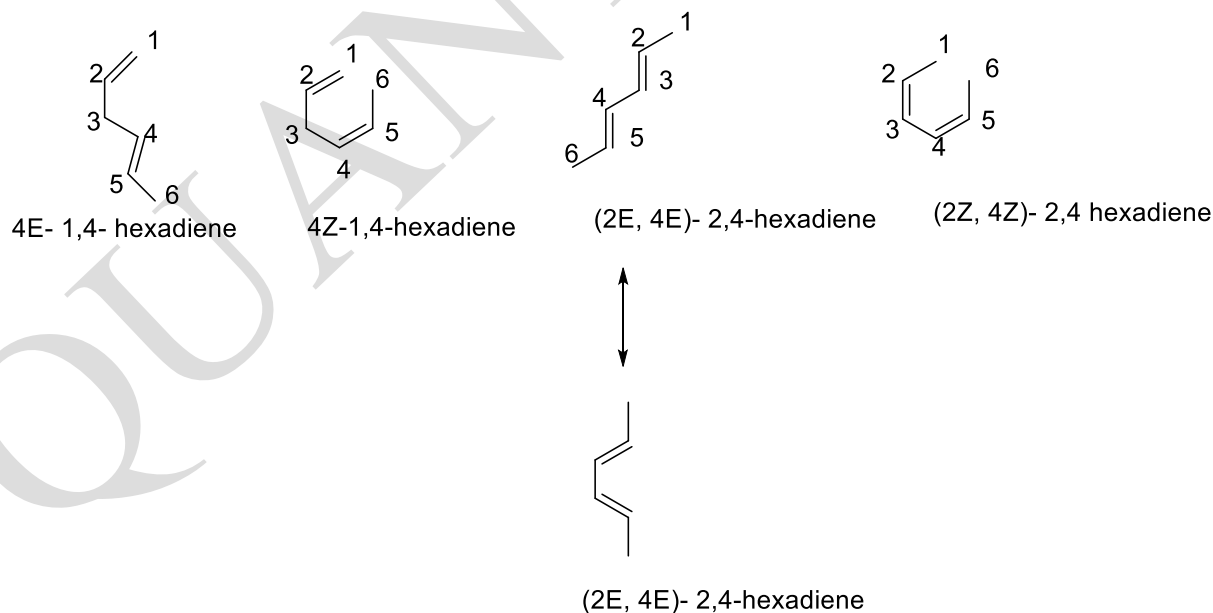
19. Correct answer: (a)

Explanation:

The mechanism of the reaction is shown below.

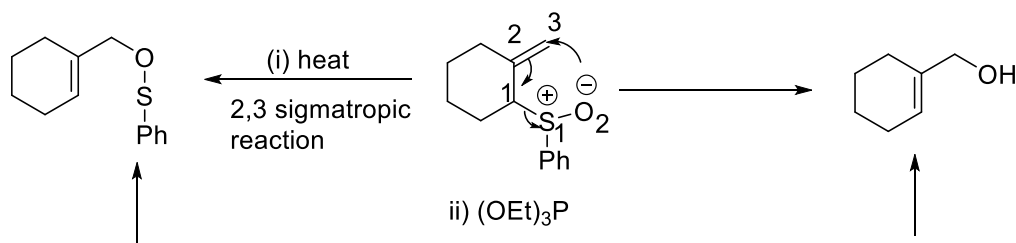
**20. Correct answer: (c)**

Explanation: The diene with s-cis configuration is the most reactive diene. Among the following, (2E, 4E)-2,4 hexadiene is the most reactive as it has a s-cis configuration.

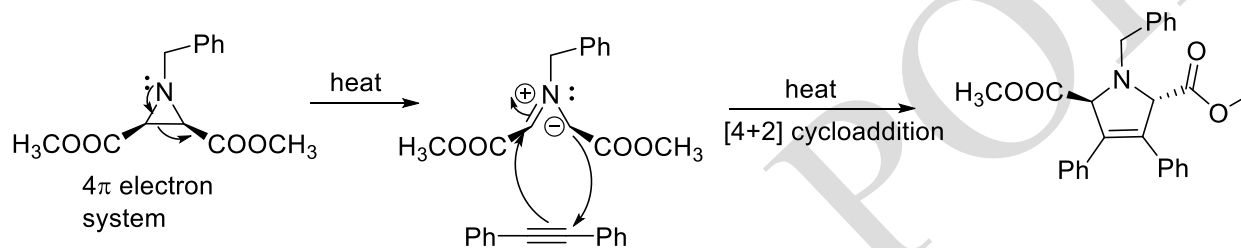


21. Correct answer: (d)

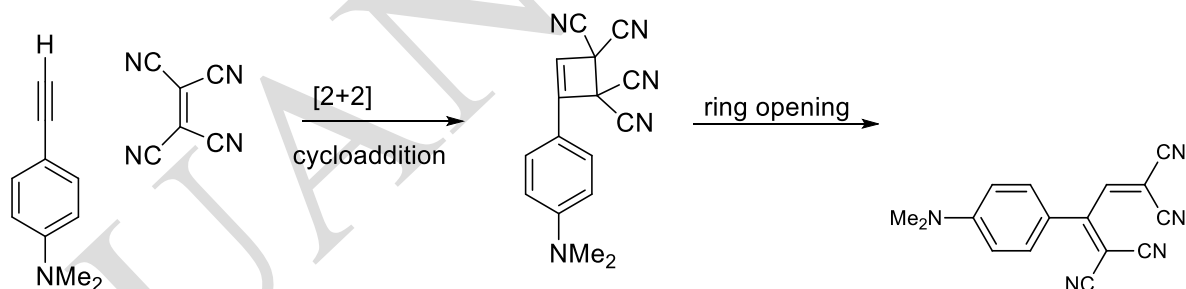
Explanation:

**22. Correct answer: (b)**

Explanation: The mechanism of the reaction is illustrated below.

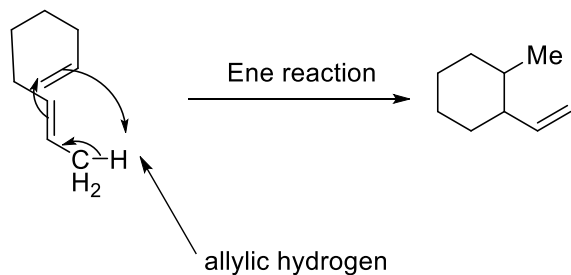
**23. Correct answer: (c)**

Explanation: The mechanism of the reaction is shown below:

**24. Correct answer: (a)**

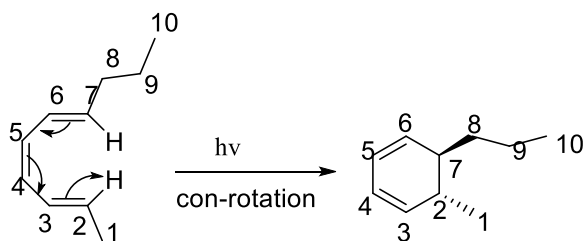
Explanation:

Ene reaction: The joining of a double bond to an alkene reactant having a transferable allylic hydrogen is called an ene reaction.



25. Correct answer: (a)

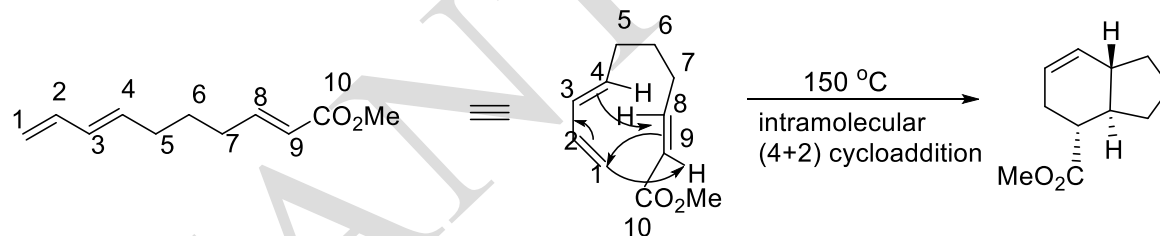
Explanation:



(2E, 4Z, 6E) decatriene

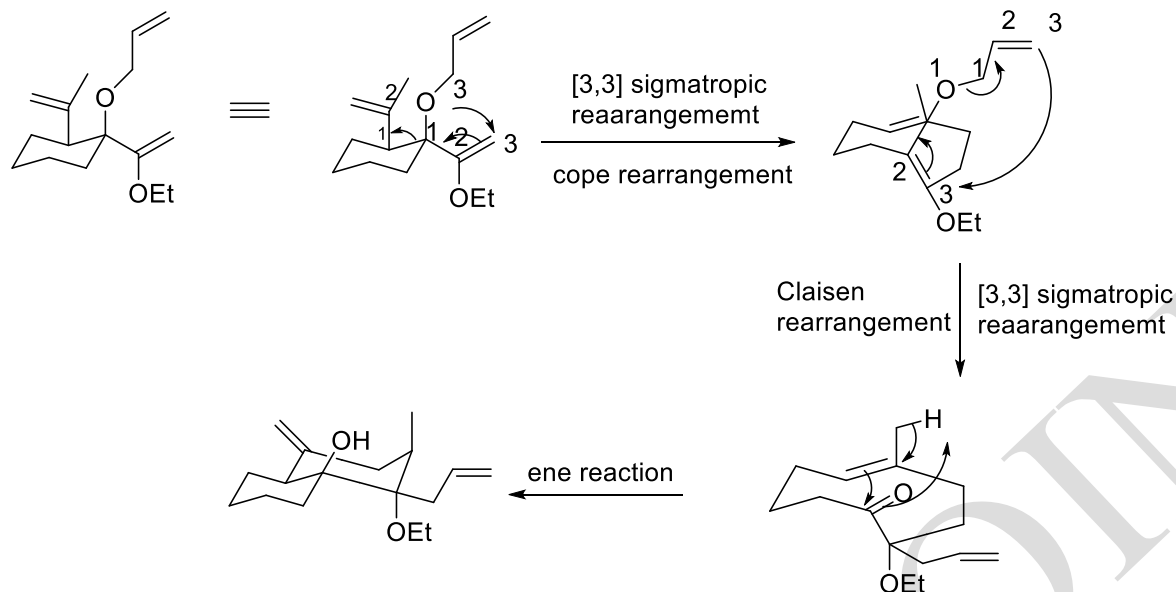
26. Correct answer: (a)

Explanation: Intramolecular cycloaddition takes place at high temperature.



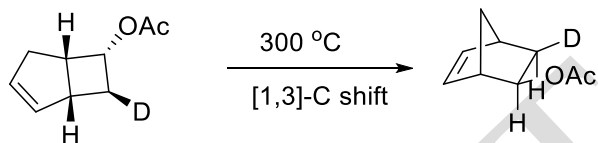
27. Correct answer: (b)

Explanation: The sequence of reaction is shown via the mechanism shown below.



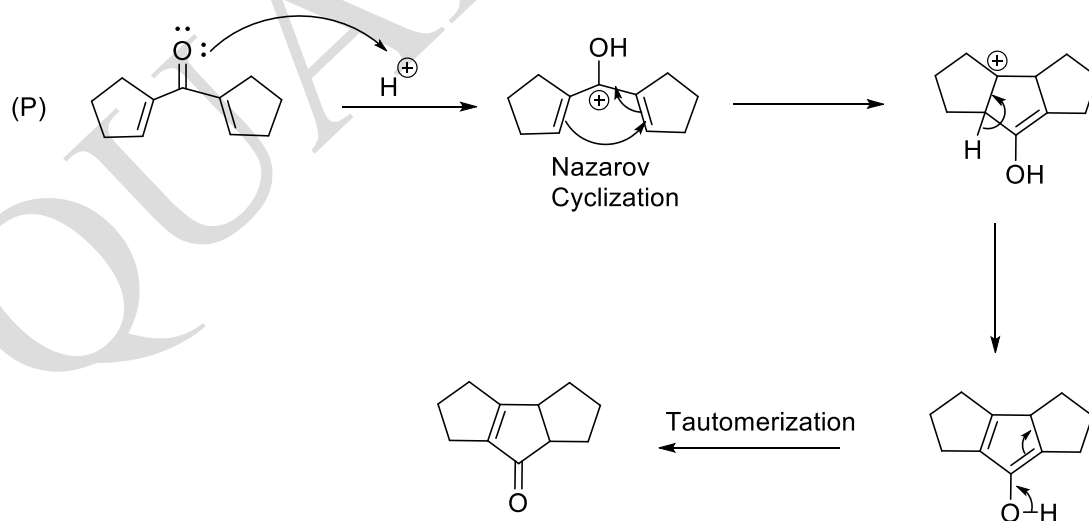
28. Correct answer: (c)

Explanation: The [1,3] allyl shift occurs antarafacially resulting in inversion of configuration. Hence D and OAc becomes cis to each other.



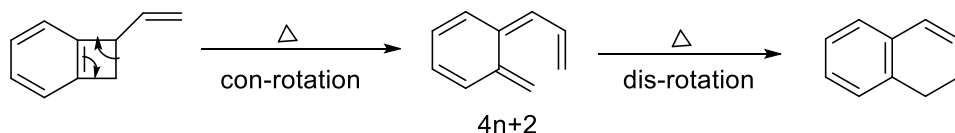
29. Correct answer: (a)

Explanation: The orbital interactions are shown below.



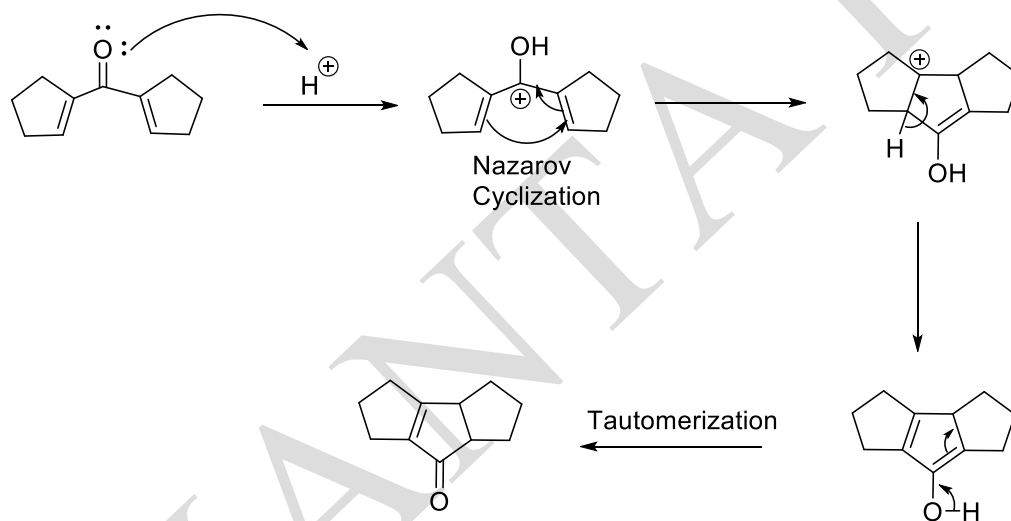
30. Correct answer: (c)

Explanation: The above transformation takes place through con-rotatory process followed by dis-rotatory process.

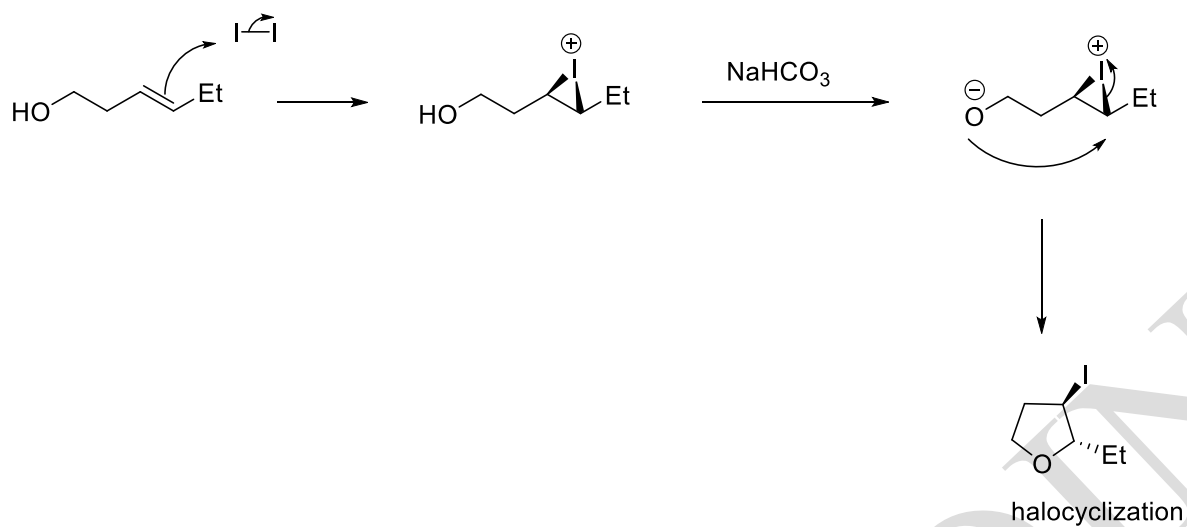
**31. Correct answer: (b)**

Explanation: The mechanism of the cyclization reactions are shown below:

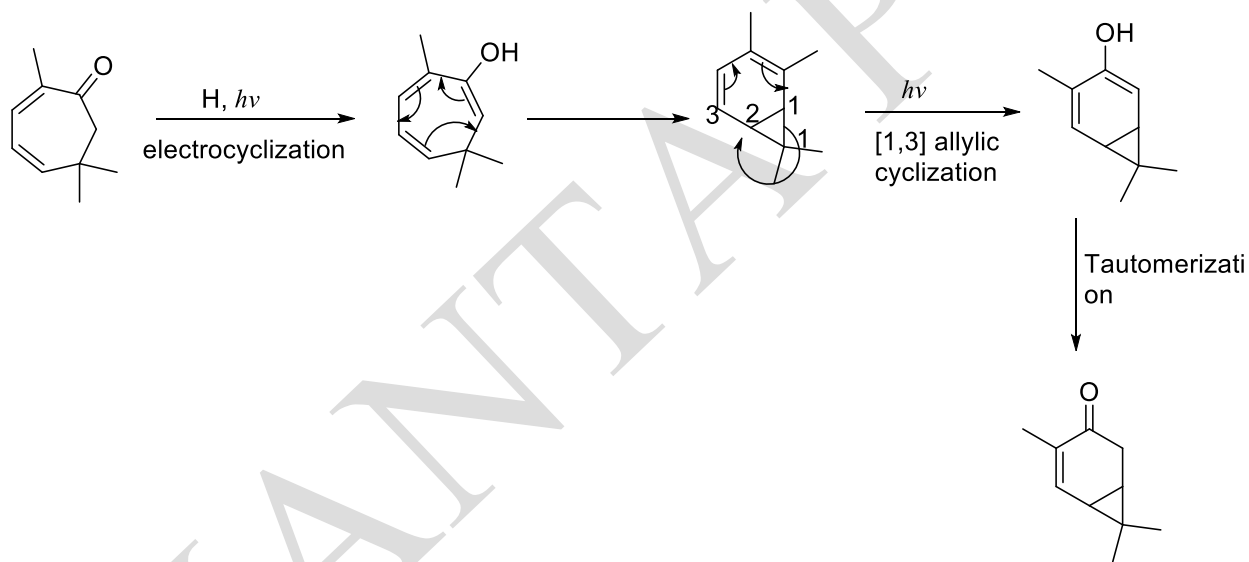
(P)



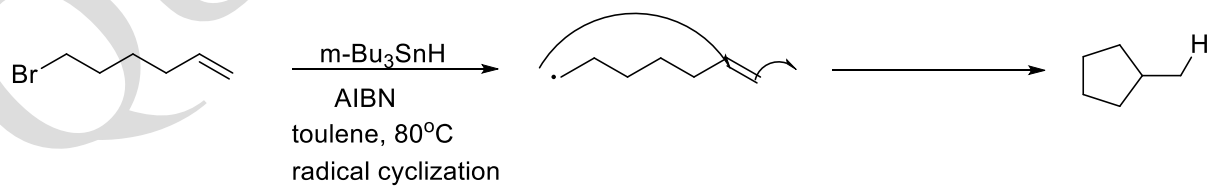
(Q)



(R)

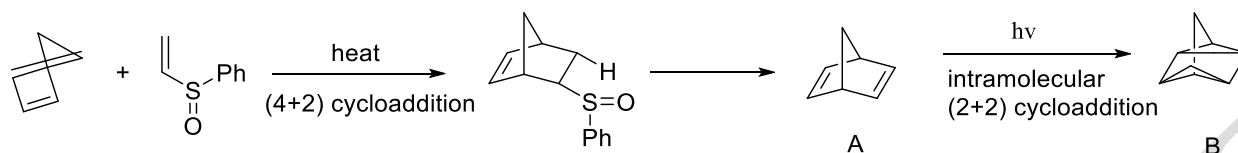


(S)

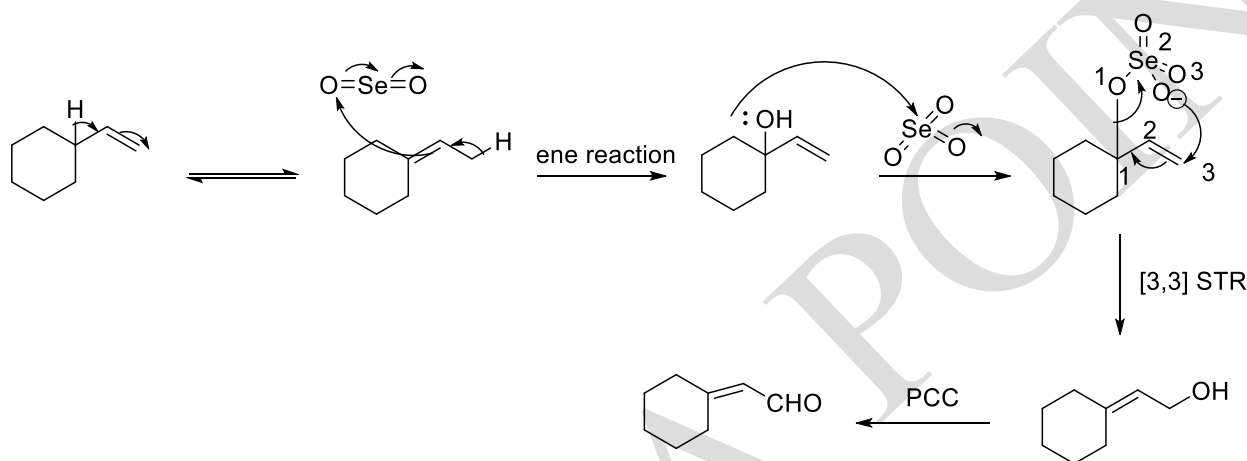


32. Correct answer: (c)

Explanation: In presence of heat, the reactants undergo diels alder reaction to give the product A. Further under photochemical condition, A undergoes intramolecular [2+2] cycloaddition to give B.

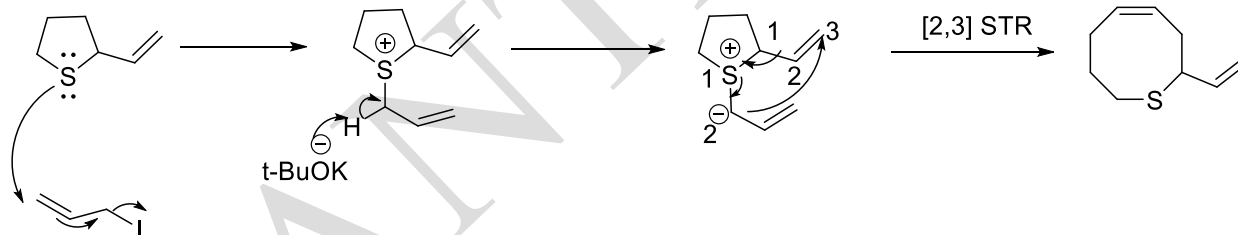


33. Correct answer: (a)



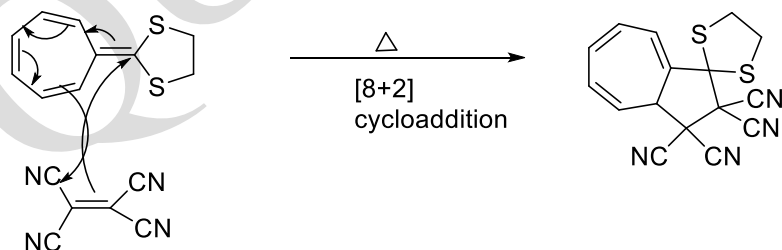
34. Correct answer: (b)

Explanation:



35. Correct answer: (d)

Explanation: The following reaction is an example of [8+2] cycloaddition.



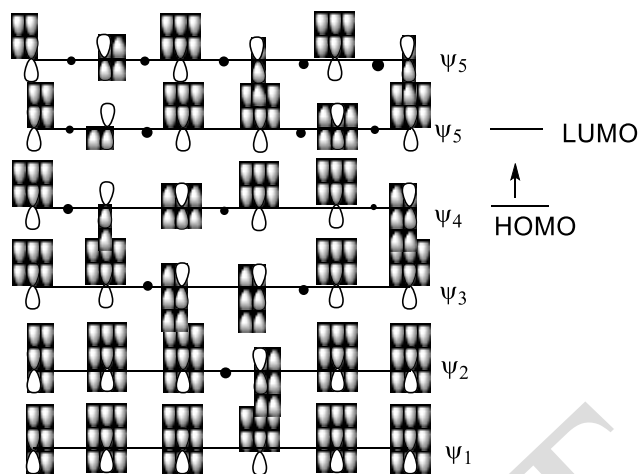
36. Correct answer: (b)

Explanation: The following reaction is an example of aza-cope followed by mannich reaction.

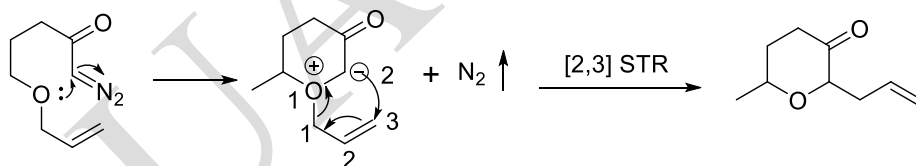
Aza cope rearrangement is [3,3] sigmatropic rearrangement reactions of nitrogen substituted 1,5 hexadienes. The final product of Mannich reaction is β -amino carbonyl compound, also known as Mannich base.

37. Correct answer: (d)

Explanation: The 6 molecular orbitals of 1,3,5 hexatriene are shown below. In photochemical condition, Ψ_4 is the HOMO and Ψ_5 is the LUMO. Under thermal conditions, Ψ_3 is the HOMO and Ψ_4 is the LUMO.

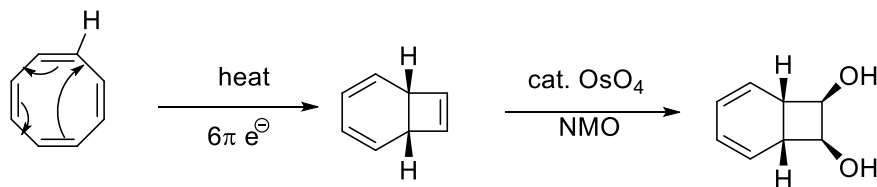
**38. Correct answer: (b)**

Explanation The mechanism of the reaction is shown below. In this reaction. Elimination of nitrogen gas is followed by [2,3] sigmatropic rearrangement.

**39. Correct answer: (b)**

Explanation:

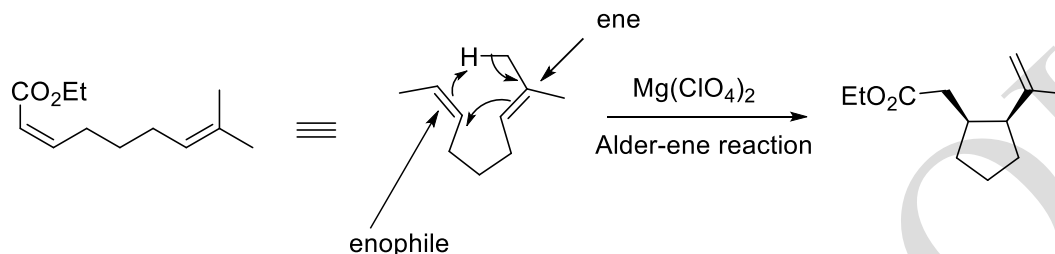
Cat. OsO_4 in presence of NMO (N-methylmorpholine-N-oxide) gives syn-dihydroxylation reaction of alkene.



40. Correct answer: (a)

Explanation:

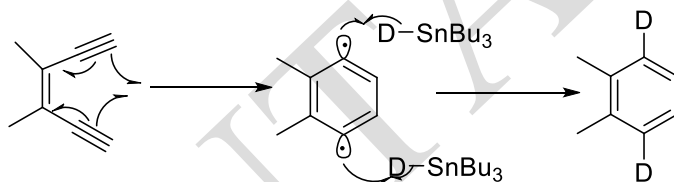
This reaction is an example of alder-ene reaction. Mechanism of the reaction is shown below.



41. Correct answer: (a)

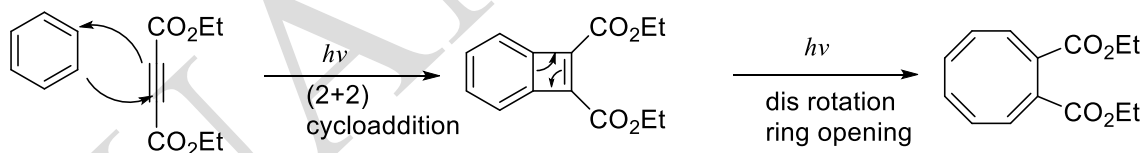
Explanation: The reactant undergoes Bergman cyclization in presence of heat to give A. In presence of deuteriated-tributyl tin hydride, A gives B following radical mechanism pathway.

Bergman Cyclization



42. Correct answer: (d)

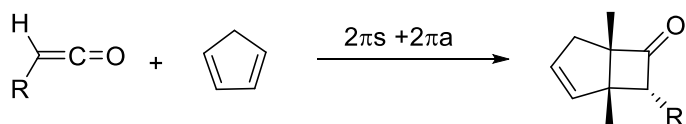
Explanation:



43. Correct answer: (b)

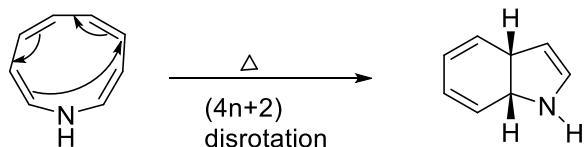
Explanation:

Bulkier the R group, higher the preference of endo product.

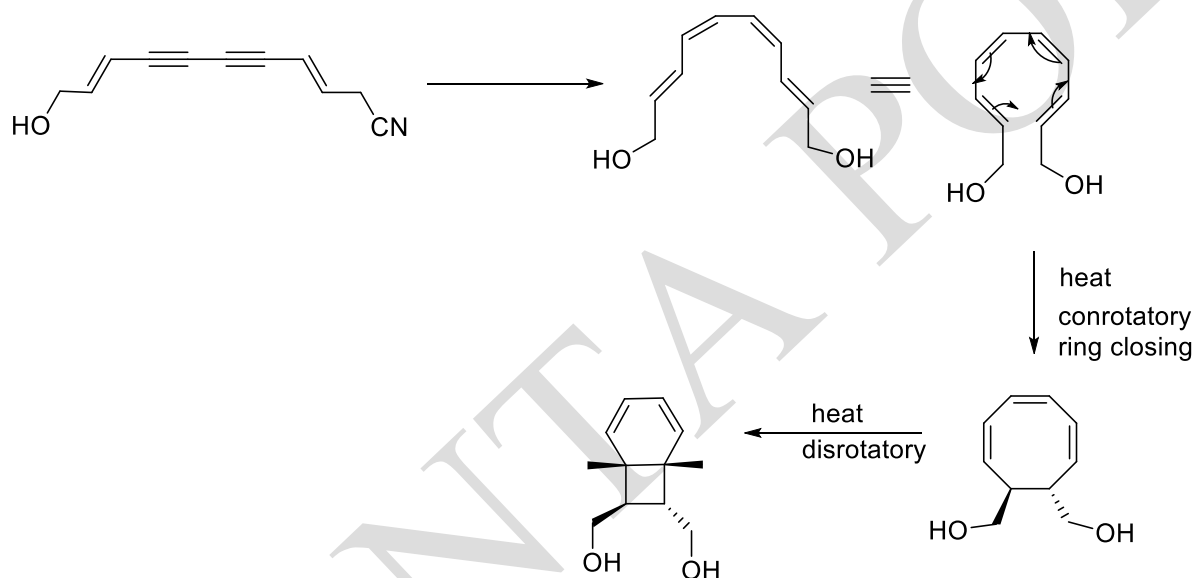


44. Correct answer: (a)

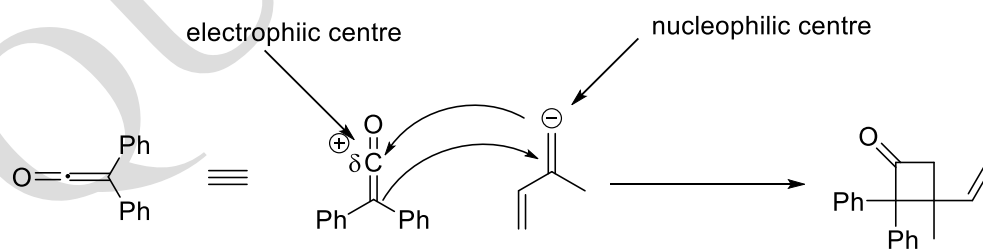
Explanation: 6π electrons ($4n+2$) undergo concerted reaction to give the product.

**45. Correct answer: (b)**

Explanation:

**46. Correct answer: (a)**

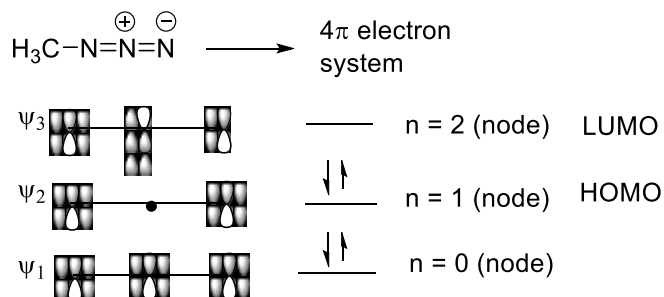
Explanation:



47. Correct answer: (b)

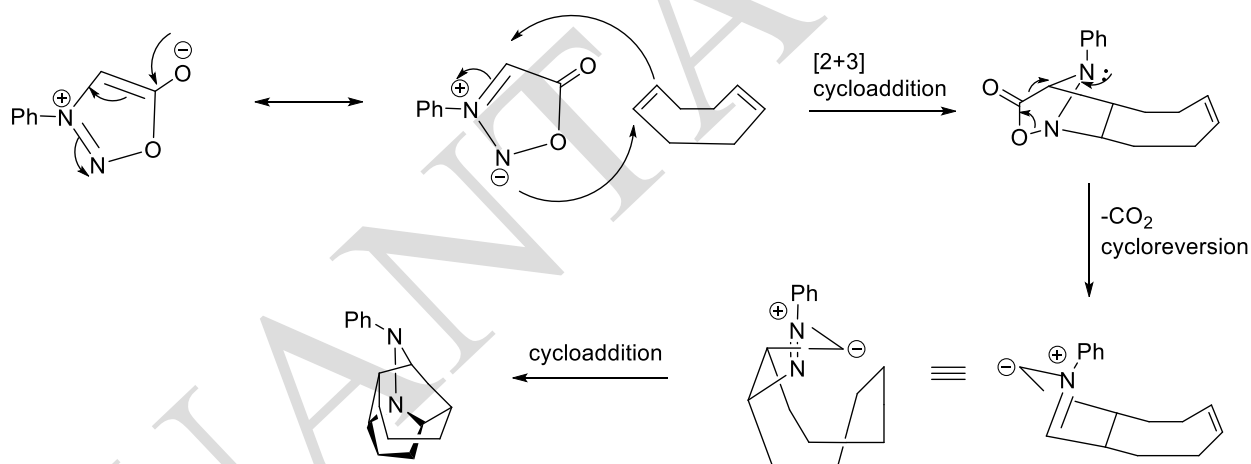
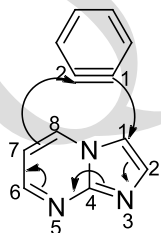
Explanation: Ψ_2 is the HOMO of π -molecular orbital of methyl azide. The π -molecular orbitals of methyl azide are shown below.

methyl azide

**48. Correct answer: (b)**

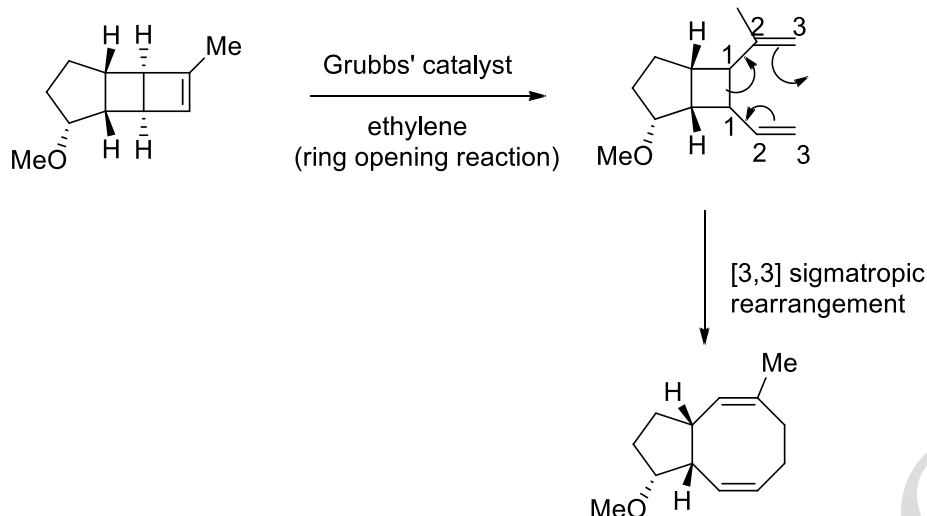
Explanation:

The mechanism of the reaction is shown below:

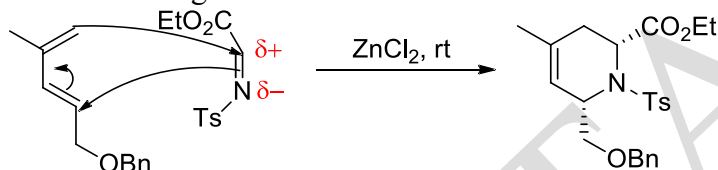
**49. Correct option (c)**

50. Correct option (d)

Mechanism is as follows

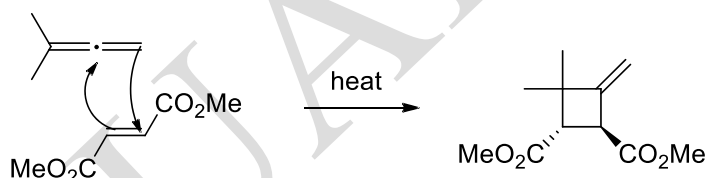
**51. Correct option (d)**

Mechanism is given as follows

**52. Correct option (b)**

Ketene, carbene and allene shows [2+2] cyclo-addition in thermal conditions, among which less sterically hindered site reacts.

Mechanism is shown below

**53. correct option (c)**

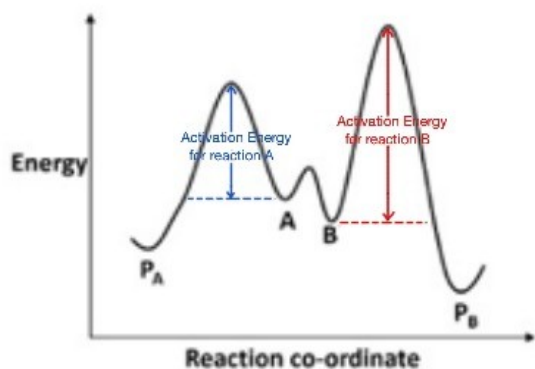
In the above reaction, among A and B, B is more stable as there is no 3-membered ring strain, hence in the energy profile diagram B must be lower than A.

For products P_A we have steric repulsion among three membered ring and alkene group, causing less stability and hence it will be above P_B, in energy profile diagram. Hence we can cancel out options (a) and (b).

Now we have to look for the activation energies of formations of P_A and P_B . Since both reactions are [4+2] cycloaddition reactions having same dienophile, the diene A will be more favoured for the reaction over B as the diene is more cisoid in case of A and hence there will be ease of product formation.

Thus reaction from A to P_A will take place much easily (hence less activation energy) than the reaction from B to P_B (have more activation energy).

Hence correct option (c)

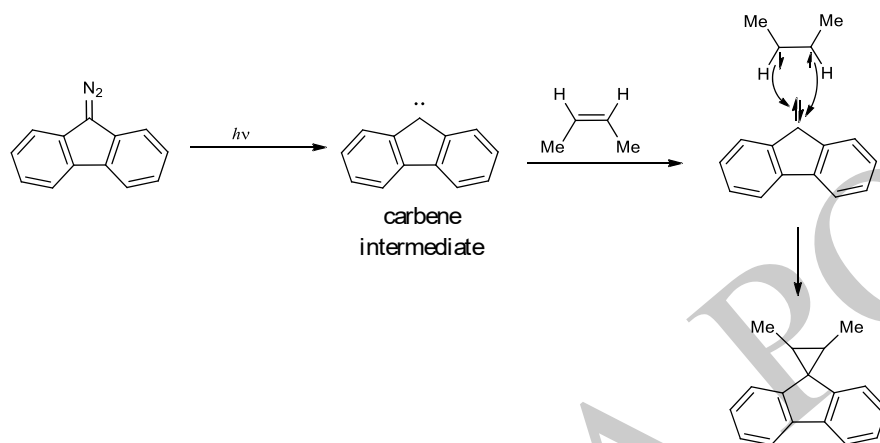


PHOTOCHEMICAL REACTIONS

HINTS & SOLUTIONS

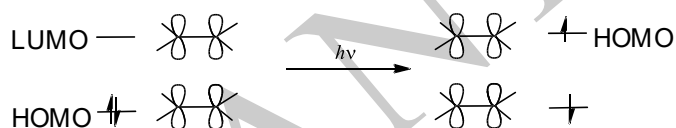
1. **Correct Answer : (d)**

Explanation :

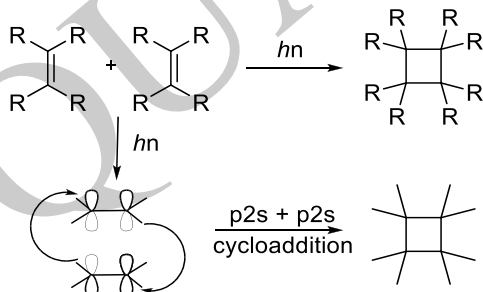


2. **Correct Answer : (d)**

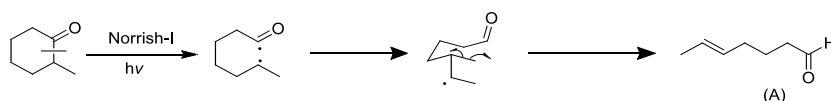
Explanation : HOMO of one alkene reacts with LUMO of other.



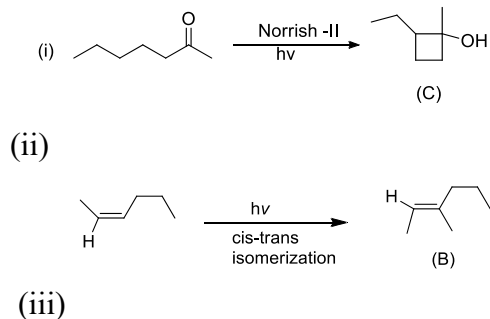
Detailed Mechanism,



3. **Correct Answer : (a)**

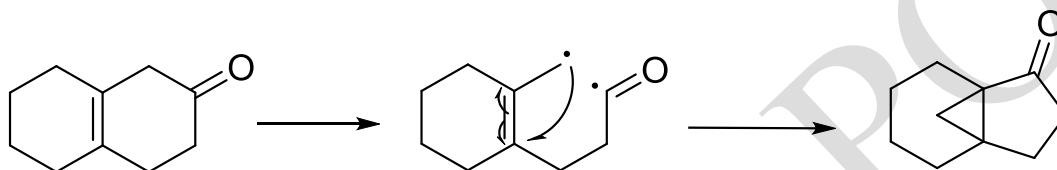


(i)



4. Correct answer: (c)

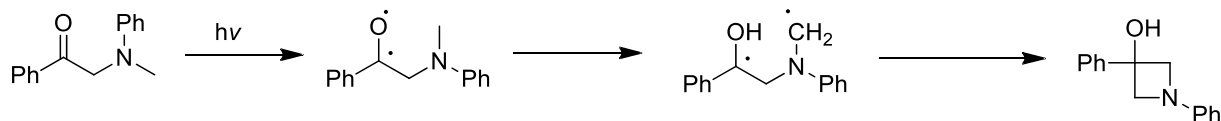
Explanation:



5. Correct answer: (b)

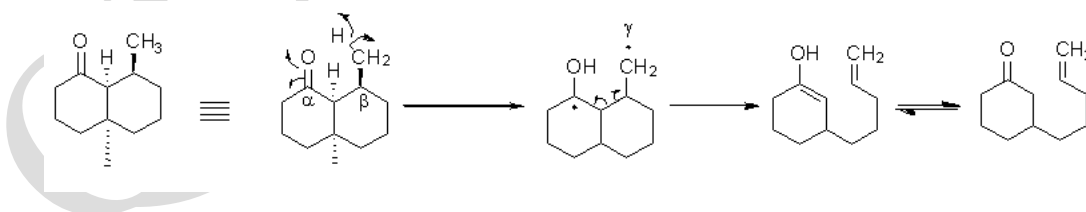
Explanation:

The above transformation goes through δ -H transfer.



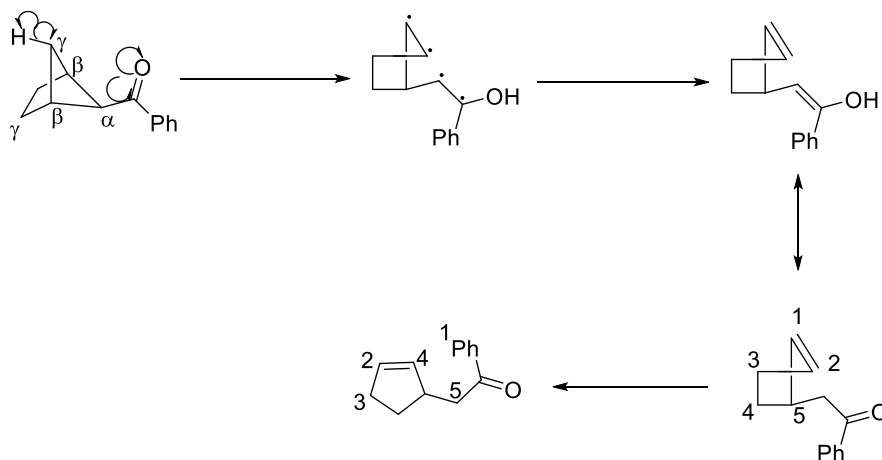
6. Correct answer: (d)

Explanation:



7. Correct answer: (b)

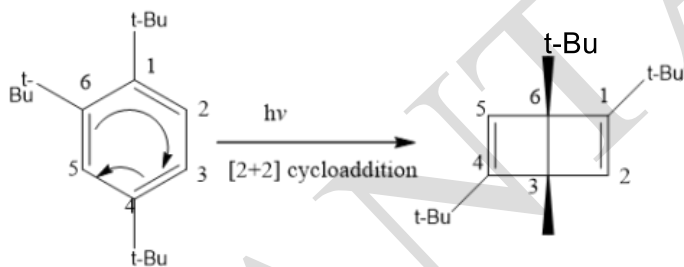
Mechanism of the reaction is shown below:



Among the two γ -hydrogens the one which is in proximity to the carbonyl group undergoes reaction.

8. Correct answer: (a)

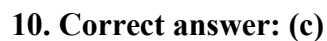
Explanation:



Note: Notice the formation of π bonds between (4-5) and sigma bonds between (6-3).

9. Correct answer: (d)

Explanation:



11. Correct answer: (a)

Reaction scheme showing the synthesis of methyl cyclopropanecarboxylate from 1,1-diazobicyclo[2.2.0]hexan-6-one:

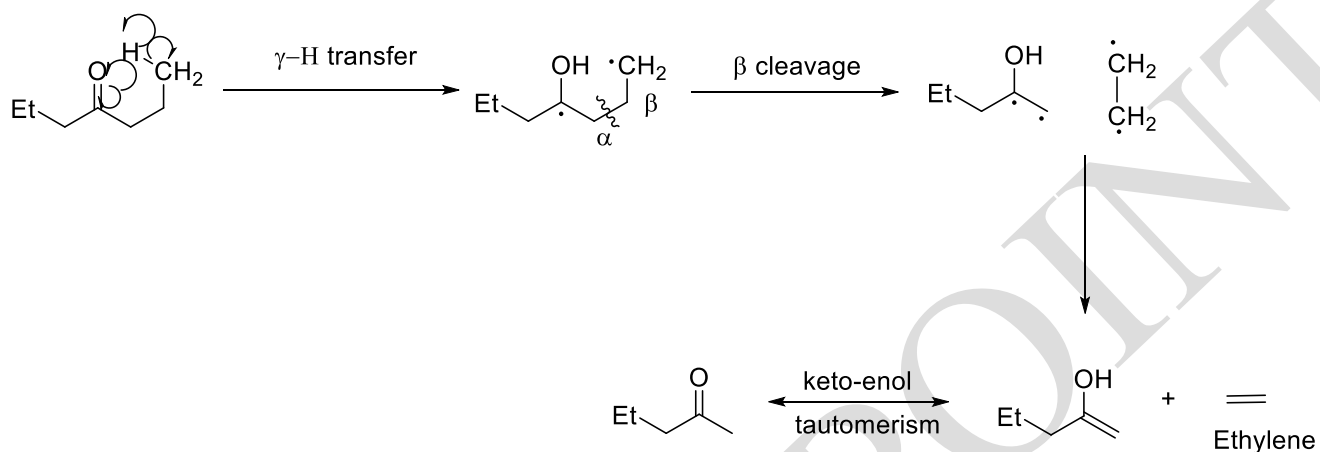
C12CCC(C1)C(=O)N=[N+]2 + MeOH --hv--> [C-]12CCC(C1)C(=O)[N+]2 + N2 --hv--> :C12CCC(C1)C(=O) + MeOH --> CO2Me

The reaction proceeds via a carbene intermediate, which then reacts with MeOH to form the final product, methyl cyclopropanecarboxylate (CO₂Me).

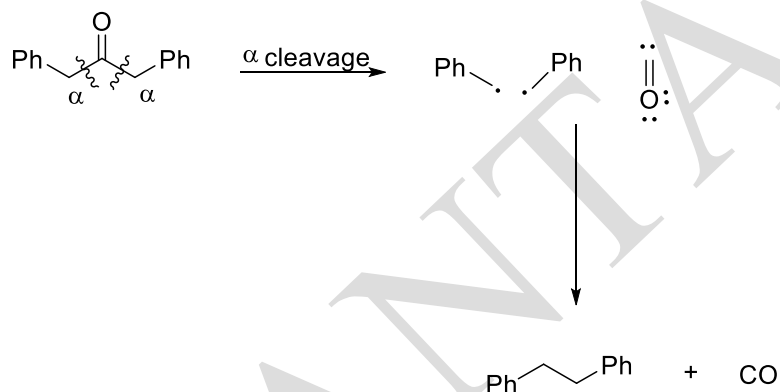
12. Correct answer: (d)

Explanation:

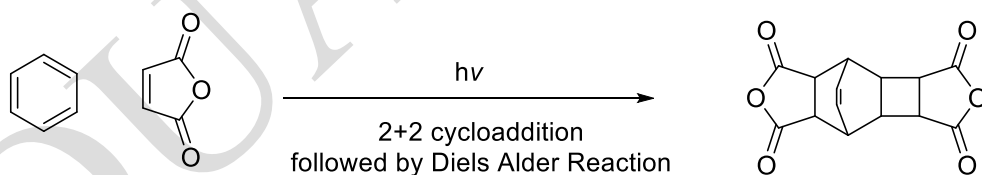
P)

 γ -H transfer followed by β cleavage is Norrish type -II process

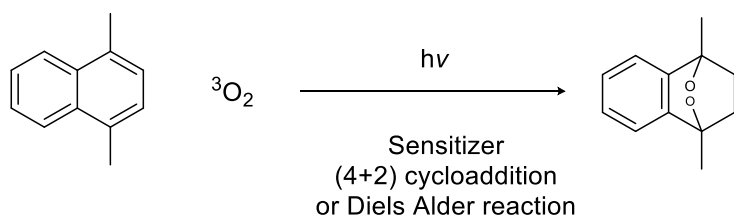
Q)



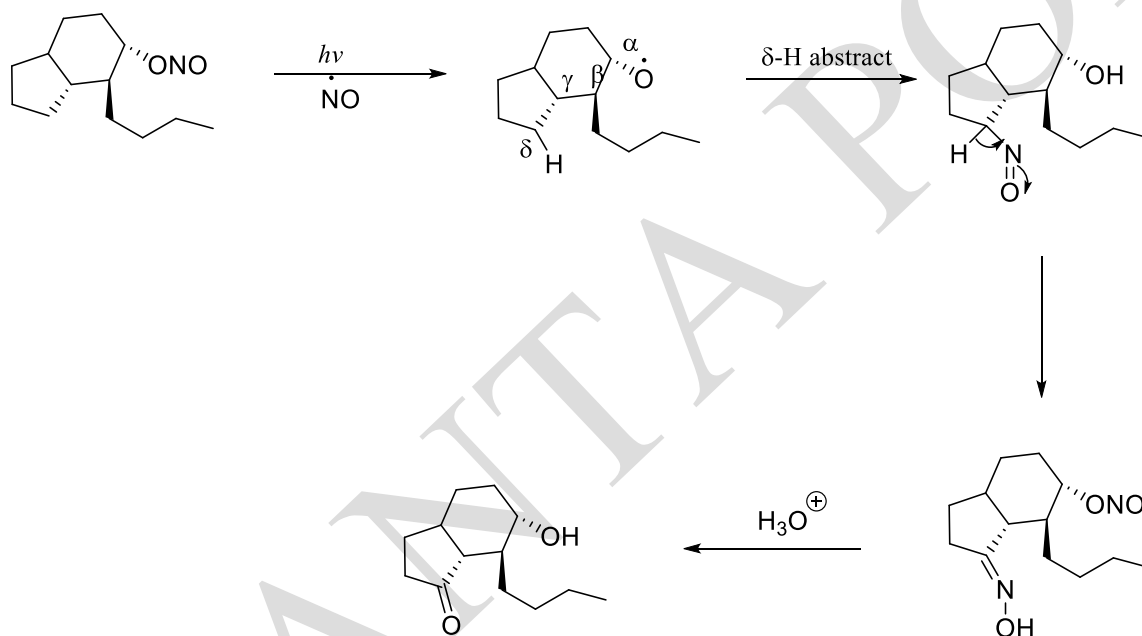
R)



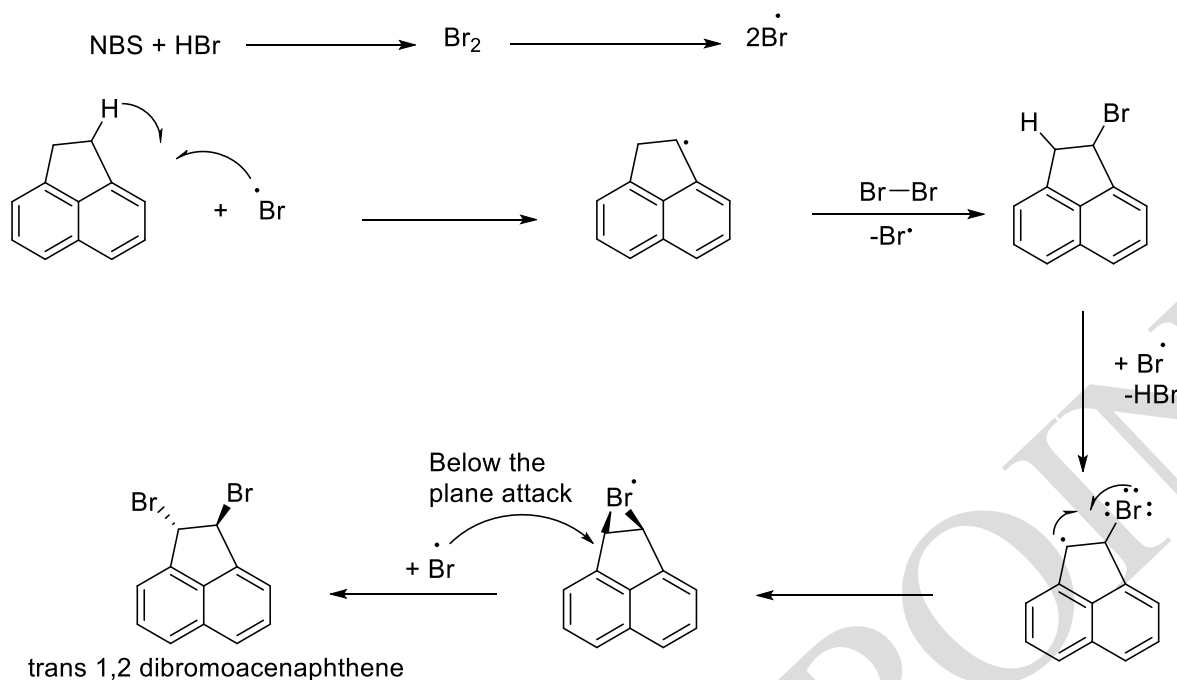
S)

**13. Correct answer: (a)**

Explanation: The following reaction is Barton reaction. The mechanism of the reaction is shown below. Barton reaction is a photochemical reaction that involves the photolysis of alkyl nitrite to form nitroso alcohol.

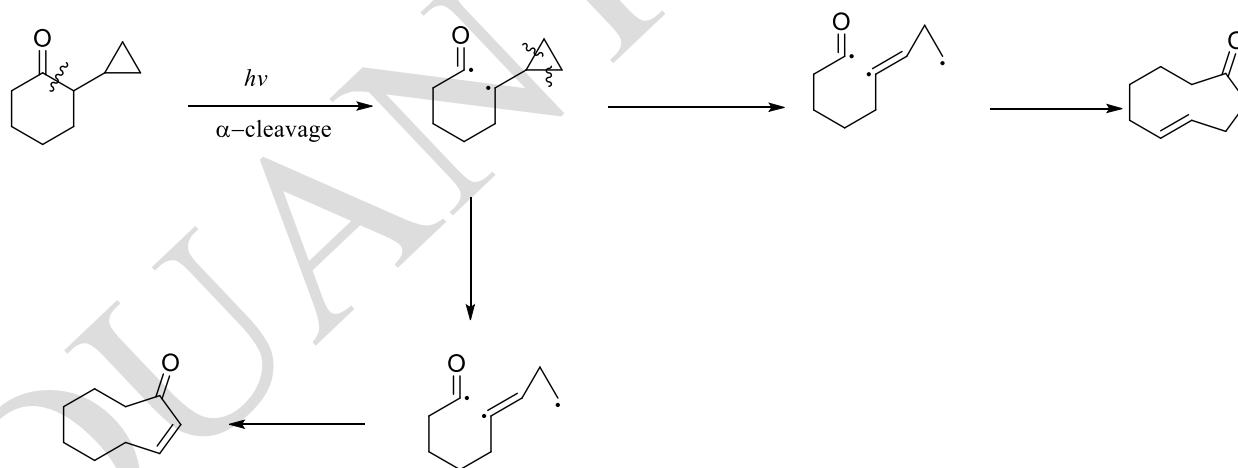
**14. Correct answer: (b)**

Explanation: The mechanism of the reaction is given below:



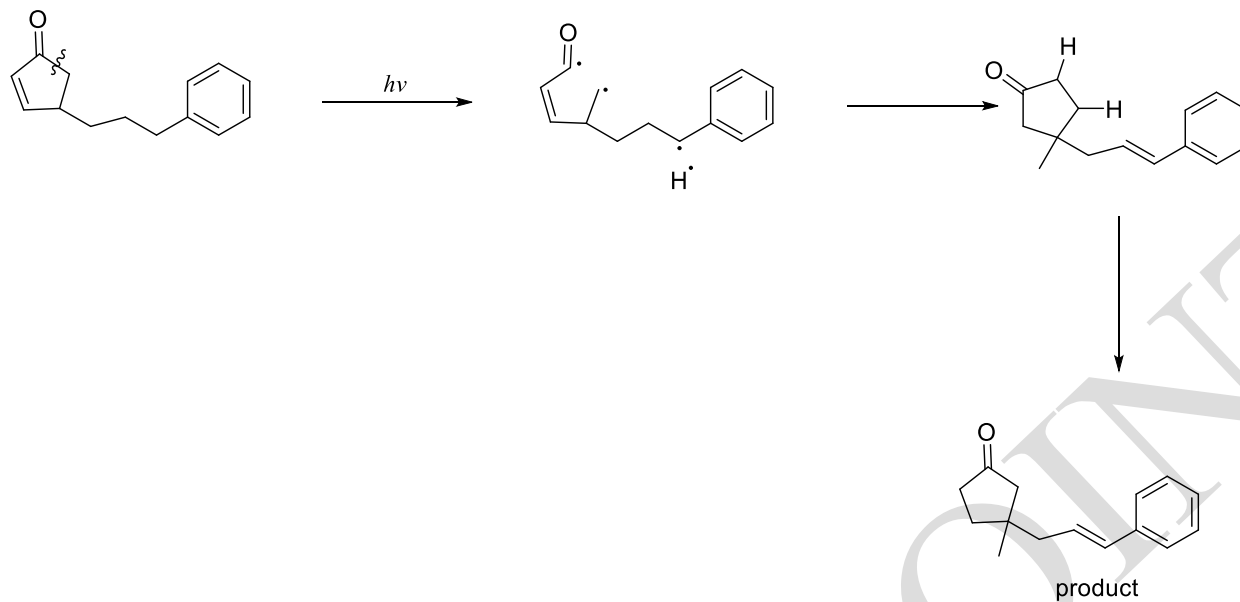
15. Correct answer: (a)

Explanation: The following photochemical reaction is Norrish type-I reaction. The mechanism of the reaction is shown below:



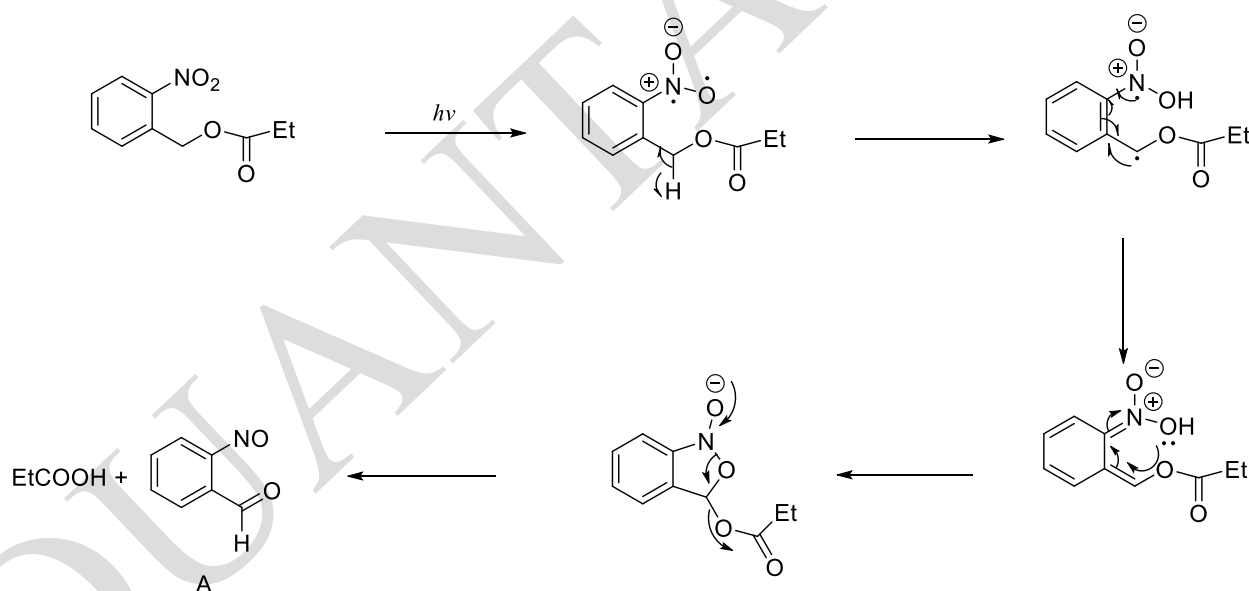
16. Correct answer: (c)

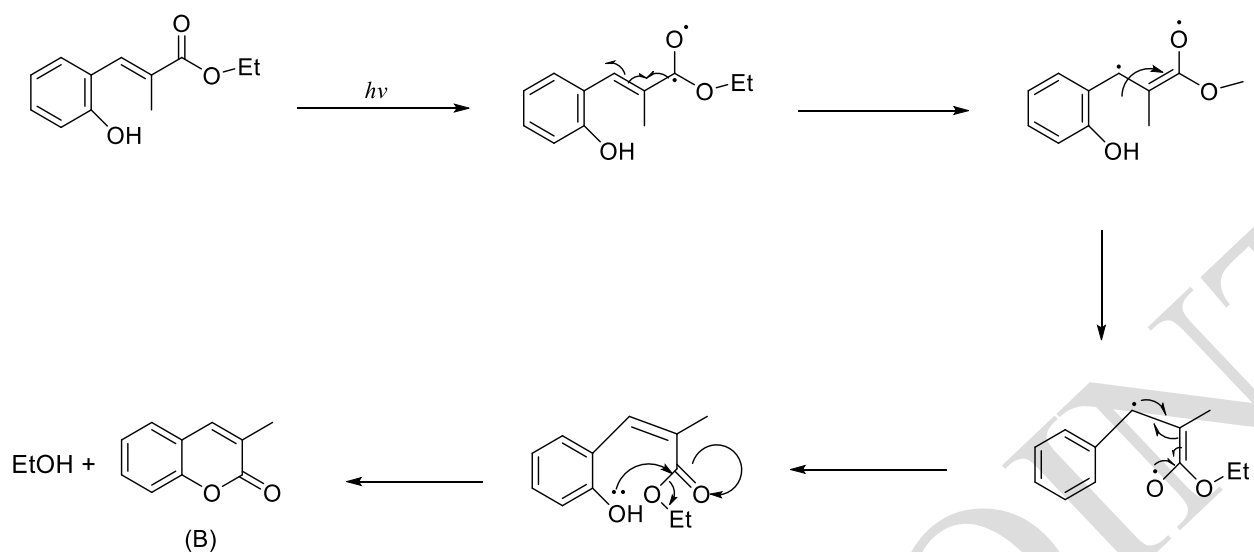
Explanation: In presence of light, benzal free radical is formed. The mechanism of the following reaction is shown below:



17. Correct answer: (a)

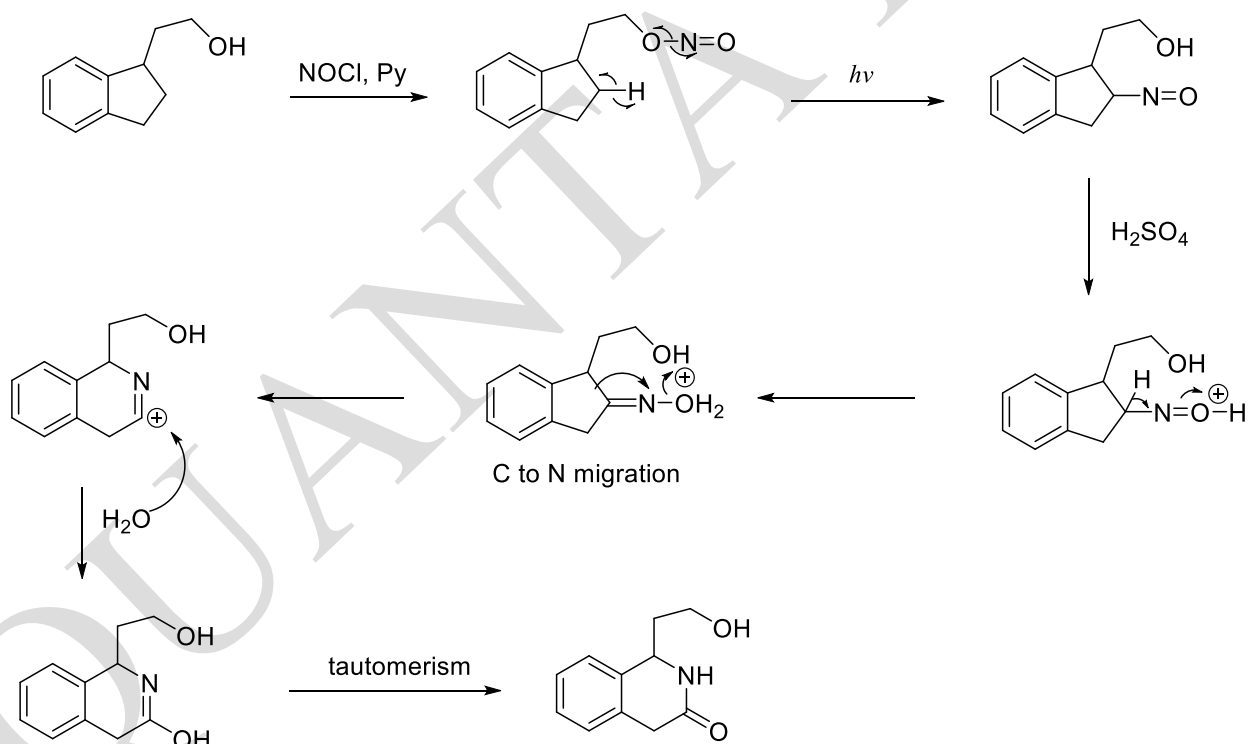
Explanation: Norrish type – II mechanism for the photo cleavage of 2-nitrobenzyl based photo labile protecting group. The mechanism is shown below:





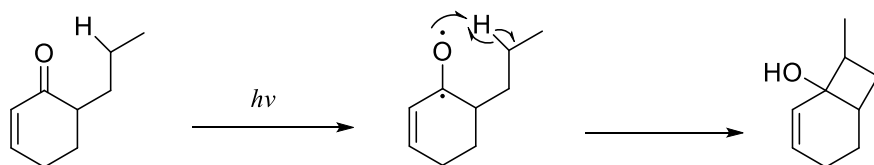
18. Correct answer: (b)

Explanation: The mechanism of the reaction is shown below:



19. Correct answer: (d)

Explanation: The mechanism of the reaction is shown below:

**20. Correct answer: (c)**

Explanation: The mechanism of the reaction is shown below:

